Abstract

Onondaga Lake, located in central New York, exhibits elevated concentrations of total mercury (Hg_T) and methyl mercury (CH_3Hg^+) in the water column, sediments and fish tissue due to historical and ongoing discharges of mercury (Hg). Total mercury (Hg_T) and methyl mercury (CH_3Hg^+) mass balances were developed for the lake, sediments and the water column. A total suspended solids (TSS) mass balance and associated Hg mass balance were also developed based on TSS data of tributaries and water column. Results indicate that tributaries including METRO and atmospheric deposition contributed 10.5 kg/year and 0.14 kg/year of Hg_T to the lake, respectively, while lake outlet and volatilization resulted in losses of 4.52 kg/year and 0.15 kg/year, respectively. Gross sedimentation and sediment burial was 48 kg/year and 47.7 kg/year, respectively. Two major sources of CH_3Hg^+ were tributaries including METRO (0.45 kg/year) and internal production in the water column (1.01 kg/year), while 0.3 kg/year Hg was discharged from the lake outlet. Gross sedimentation and sediment burial of CH_3Hg^+ were 1.92 kg/year and 0.2 kg/year, respectively. Moreover, an additional Hg budget was developed using empirical relationships between Hg and TSS in tributaries, water column, sediment trap and surface sediment. It appears that the major source of Hg to the water column of Onondaga Lake is resuspension of Hg deposited to sediments.

Mercury concentrations were measured in phytoplankton, zooplankton, planktivores, omnivores and piscivores. The percentage of Hg_T occurring as CH_3Hg^+ generally increased with higher trophic levels, confirming that CH_3Hg^+ is more efficiently transferred to higher trophic levels than Hg_T^{2+}. Concentrations of CH_3Hg^+ and

bioaccumulation factors (BCF) increased with higher trophic levels in aquatic species of

Onondaga Lake.

The Regional Mercury Cycling Model (R-MCM) was calibrated to Onondaga Lake and applied to evaluate various scenarios. Mass balance predictions suggest that model predictions of Hg concentrations in the water column, sediments and fish are sensitive to inputs of Hg_T mainly originating from sediments. Methyl Hg is mainly derived from internal production. Model calculations suggest how changes in physical and chemical characteristics that occur in the future affect the concentrations of Hg in the lake.

The Processes Regulating the Concentrations of Hg_T and CH_3Hg^+ in the water column, sediments and fish of Onondaga Lake, New York.

By

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THESIS

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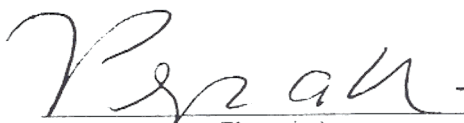(Please sign)

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Chapter 1 - Introduction

1.1 Mercury in the Environment and Mercury Cycle in Aquatic Ecosystems

Mercury (Hg) undergoes many transformations and exhibits different species in the environment, including elemental Hg (Hg^0), ionic mercury (Hg_T^{2+}), monomethyl Hg (CH_3Hg^+) and dimethyl Hg (($CH_3)_2Hg$) (Brinckman et al., 1982; Lindqvist et al., 1984). Contamination of soil, sediment or water with elevated concentrations of Hg is a serious and complex environmental problem because of the difference chemical characteristics and bioavailability of these species.

The current world production of Hg is about 9000 tonnes/year (http://www.chem.ualberta...plambeck/p102/p02264.htm). Mercury is a natural component of coal, peat and natural gas, and thus combustion of these fuels lead to Hg emissions. In addition to fossil fuels, waste incineration, chlor-alkali production, crematory incineration and the use of certain pesticides also result in Hg emissions (Lindqvist et al., 1991). Mercury is also emitted from natural surfaces such as forest soils, freshwater lakes (Xiao et al., 1991) and the open ocean (Fitzgerald, 1986). The major use of Hg through about 1970 was by the chlor-alkali industry. Mercury deposition peaked in the 1960s and 1970s, at least upper Midwest of the United States (Enstrom and Swain, 1997). In recent years the use of Hg has declined due to environmental concerns over Hg contamination. Best estimates to date suggest that human activities have about doubled or tripled the amount of Hg in the atmosphere from prior to the Industrial Revolution to today, and the atmospheric burden is increasing by about .5 percent per year (http://wwwdwimdn.cr.usga.gov/widocs/pubs/factsheets/FS216/FS_216-95.htm)

Modern measurements of atmospheric Hg concentration and deposition together with historical records from lake sediments and peat indicate that the global reservoir of atmospheric Hg has increased by the factor of 2-5 since the beginning of the industrialization period (Enstrom and Swain, 1997). In addition to concern over widespread Hg contamination by atmospheric emissions and atmospheric deposition, aquatic ecosystems can experience very high inputs of Hg associated with industrial processes such as chlor-alkali facilities, pulping operations, mining, metallurgical plant processing and the production of antifungicides.

The Hg cycle in aquatic ecosystems is complicated because of the myriad of species and pathways. However, our understanding of the biogeochemistry of Hg has increased markedly over last several years (Driscoll et al., 1994). Atmospheric deposition of Hg occurs largely as Hg_T^{2+} (Winfrey and Rudd, 1990), although inputs of CH_3Hg^+ also occur (Bloom and Watras, 1989). Mercuric ion (Hg_T^{2+}) will complex with inorganic ligands such as Cl^- and OH^-, bind with dissolved organic carbon (DOC), or sorb to particulate matter within oxygenated waters (Driscoll et al., 1994). Mercuric ion can be reduced microbially or abiotically to form Hg^0. Since most waters are oversaturated with respect to the solubility of atmospheric Hg^0, Hg^0 is readily volatilized to the atmosphere (Vandal et al., 1991). Within the anoxic zones, Hg forms strong aqueous complexes with sulfide and precipitates as HgS (Driscoll et al., 1994; Wang and Driscoll, 1995). Mercuric ion can also be methylated to CH_3Hg^+ within the anaerobic environments. Sulfate-reducing bacteria appear to be important in the methylation of Hg (Compeau and Bartha, 1985; Gilmour et al., 1992). Methyl Hg (CH_3Hg^+) may bind to DOC, Cl^-, sulfide and other complexing ligands. Methyl Hg is also demethylated by

microbial processes (Driscoll et al., 1994), producing Hg^0 as a byproduct. Methyl Hg is the form of Hg that largely bioconcentrates in aquatic biota (Grieb et al, 1990; Mason et al, 1995).

Methyl Hg is the most critical form of Hg, because it is highly toxic and readily accumulates in fish (Bloom, 1992). It was found that methylation may occur in the water column (Furutani and Rudd, 1980), in the external slime layer of fish (Jernelov, 1972) and the intestinal contents of fish (Rudd et al., 1983). Studies have shown that flooded terrestrial surfaces, including wetlands (Driscoll et al., 1994; St. Louis et al., 1994; Hecky et al., 1991) are important sites for production and supply of CH_3Hg^+ and to freshwater ecosystems and reservoirs.

Fish and other organisms accumulate CH_3Hg^+ to higher concentrations than found in surrounding waters, because CH_3Hg^+ is absorbed from water by organisms. Methyl Hg concentrations in water are generally very low (< ng/L), and constitute a small fraction (< 20 %) of the total Hg content of most natural waters. Historically it was thought that fish and shellfish selectively retain CH_3Hg^+ in preference to Hg_T^{2+}, mainly because CH_3Hg^+ is much more lipophilic than Hg_T^{2+} (Stolzenburg et al., 1986). However, Mason et al. (1995) indicate that this explanation is inadequate because Hg_T^{2+} complexes, which are not bioaccumulated, are as lipid soluble as their CH_3Hg^+ analogs. Moreover, unlike other hydrophobic compounds, CH_3Hg^+ resides in protein rather than fat tissue in fish (Mason et al., 1995). Mason et al (1995) showed that uptake of Hg_T^{2+} and CH_3Hg^+ by phytoplankton resulted in higher concentrations of both species in tissue. However, within phytoplankton cells Hg_T^{2+} is principally membrane bound, while CH_3Hg^+ accumulates in the cytoplasm. This difference in the partitioning of Hg within

phytoplankton leads to a greater assimilation of CH_3Hg^+ during zooplankton grazing. The CH_3Hg^+ associated with phytoplankton cytoplasm is readily ingested by zooplankton, while Hg_T^{2+} is not readily assimilated and largely excreted. Thus the discrimination of Hg_T^{2+} and CH_3Hg^+ occurs during trophic transfer and enrichment occurs between water and phytoplankton (Mason et al., 1995). Virtually all of the Hg found in muscle tissue of fish is as CH_3Hg^+ (Greib et al., 1989; Bloom, 1992). Because of the bioaccumulation of CH_3Hg^+ that occurs via the aquatic food chain, the exposure of CH_3Hg^+ by humans is primarily through the consumption of fish rather than through drinking water (USEPA, 1980; Gloss et al., 1990).

1.2 Health Effects of Mercury

Humans are largely exposed to Hg by two pathways: (1) as CH_3Hg^+ from fish consumption, or (2) by inhaling vaporous mercury (Hg^0) Elemental Hg (Hg^0) does not usually cause illness when ingested; however, when Hg^0 is inhaled at levels below   mg Hg/m^3, non-specific symptoms may be evident, including shyness, insomnia, anxiety and loss of appetite (Milne et al., 1970). At concentrations between   and 3 mg Hg/m^3 (Milne et al., 1970), headaches, salivation, metallic taste, chills, breathing difficulties, coughs, tremors, cramps, diarrhea, nausea, vomiting, tightness in the chest, fatigue and lung irritation may occur. Exposure to higher concentrations may produce flu-like symptoms and pneumonia, which may result in death in severe cases.

The major human health effects of CH_3Hg^+ are neurotoxicity in adults (Bakir et al., 1993), and toxicity of the fetus of mothers exposed to this species during pregnancy (Cox et al., 1989). Clinical manifestations of neurotoxic effects are: paresthesia, a

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numbness and tingling sensation around the mouth, lips and extremities, particularly the fingers and toes; (2) cerebellar ataxia, a staggering gait and postual imbalance; (3) neurasthesia, an abnormal condition characterized by nervous exhaustion, vague functional fatigue and inability to concentrate; (4) dysarthria, difficulty in articulating speech; (5) concentric constriction of the visual fields and hearing loss; (6) difficulty in swallowing, and progressive intellectual deterioration; (7) distal hypaesthesia, disturbances of superficial and deep sensations; (8) spasticity and tremor; and (9) coma and death (Jugo, 1979; Goyer, 1991).

Methyl Hg is of particular importance as a water quality parameter, since this form is highly toxic and it readily accumulates in fish (Grieb et al., 1990; Bloom, 1992). Ingestion of CH_3Hg^+ in fish is the primary pathway of human exposure to Hg.

Due to concerns over health effects associated with exposure to eleavted levels of Hg, the U.S. Food and Drug Administration (FDA) has set a limit of 1 μg/g (ppm) for concentrations of Hg in fish sold in interstate commerce. Canada and several U.S. states have developed consumption advisories of 0.5 μg/g for Hg in fish (Driscoll et al., 1994). Many states, including New York State, have established Action Levels at the FDA μg/g standard. Fishing advisories have been issued in most states due to elevated concentrations of Hg. Mercury contamination is widespread among surface water in eastern Canada, the United States (Figure 1.2).

1.3 Mercury Contaminated Sites

Mercury is a toxic substance. Because it readily bioaccumulates in the aquatic food chain, relatively low concentrations may result in exposure of humans to high
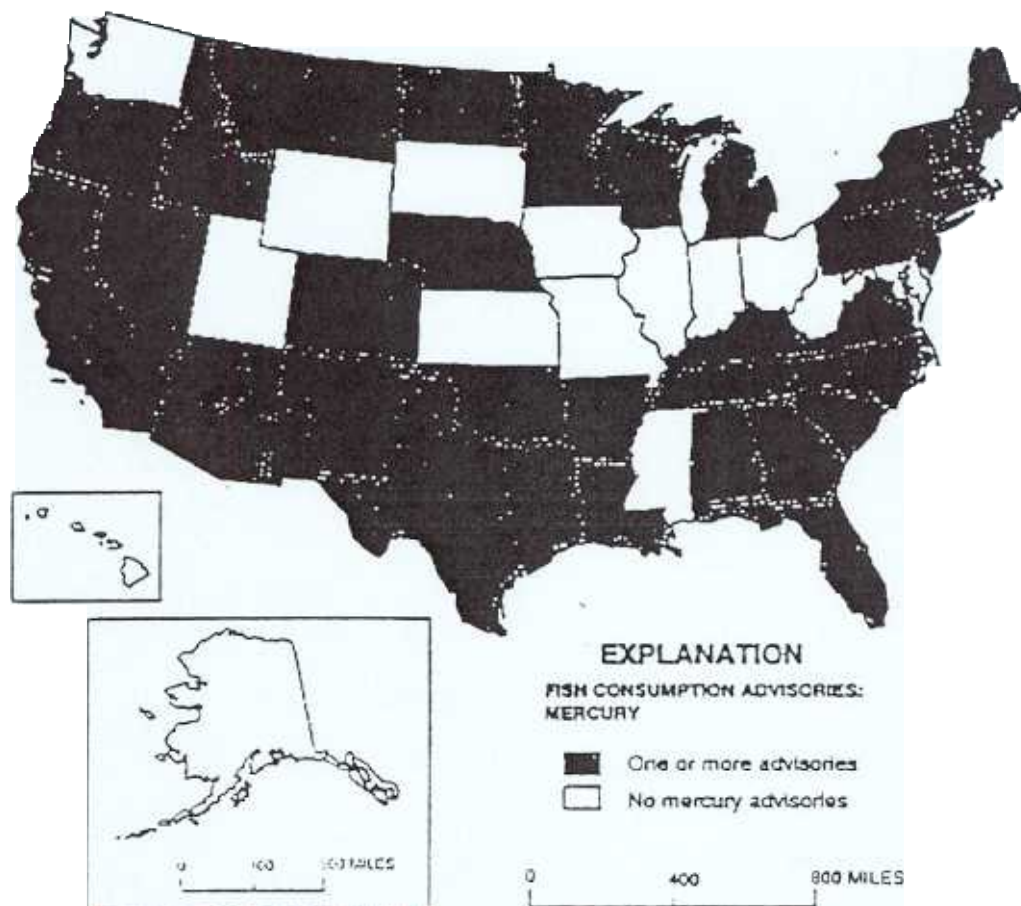
Figure 1.2 States with at least one fish consumption advisory for mercury (after USEPA Consumption Data Base)

concentrations through consumption of fish. There have been several recorded instances of Hg poisoning through industrial contamination. The most well-known of these occurred at Minimata Bay, Japan, in 1952. Historically, people in this region relied extensively on fishing for food. In the 1950's the bay received an industrial waste discharge (from a PVC (Polyvinyl Chloride) production company) containing elevated concentrations of Hg. This Hg was largely deposited to the sediments of the bay. Due to this contamination, 397 people were known to have been affected by the consumption of Hg contaminated fish. Sixty-eight people died as a result of Hg poisoning; of those affected, 22 were unborn children. The CH_3Hg^+ from contaminated oceanic water was absorbed by fish and shellfish. Concentrations of Hg in fish tissue in Minimata Bay in 1952 were 5 – 10 $\mu g/g$. The Hg concentrations in the bay and the sea water were measured in 1985 ranging from 125.3 ng/L at the center of the bay to 22.1 ng/L at the mouth of the bay towards to open ocean (Kudo and Miyahara, 1991).

The Carson River is a U.S. Environmental Protection Agency superfund site in western Nevada, USA. Mill processing of silver and gold ores in the area resulted in the release of 6.8×10^6 kg of Hg between 1859 and 1890 (Mach et al., 1996). Contaminated tailings have since eroded from the abandoned mill sites and redistributed along more than 100 km of the Carson River Valley, contaminating extensive areas. Concentrations of total Hg and CH_3Hg^+ were elevated in water and sediments downstream from the historic mill sites. Total Hg concentrations ranged from 21-3140 ng/L in water and 0.6-3.4 $\mu g/g$ in sediment downstream from the mill sites, compared to 1.2 –17 ng/L in water and 0.003-0.006 $\mu g/g$ in sediment at background locations. Concentrations of CH_3Hg^+ in the water were also high (0.25-19 ng/L). Transport of Hg in the river was largely

associated with suspended solids, and mass transport of all Hg species was greatest during May when high flows result from snowmelt in Sierra Nevada mountains.

The Wabigoon/English River–Lake system is located in an area of substantial clay deposits on the Canadian Shield of northwestern Ontario. Between 1962 and 1970, approximately 10 tonnes of Hg_T^{2+} were released into the Wabigoon River from a chlor-alkali plant - paper mill complex. Although Hg outputs were reduced between 1970 and 1975, when the use of Hg in the plant was discontinued, small amounts of residual Hg continue to be discharged into the river (Jackson et al., 1982). The system was studied by Parks et al. (1986) ten years after the Hg loadings from the plant were sharply reduced. The average Hg_T concentration in 1978 in depth integrated samples from the Wabigoon River was 41 ng/L, with 21 ng/L occurring as dissolved Hg. The mean annual Hg concentration at the paper mill effluent was 194 ng/L. From August 1978 to July 1979, the Hg_T concentrations in the rivers and lakes of the entire system ranged from 1.5-48 ng/L. During the period July 1979-June 1980, the concentration range of Hg_T was 2.5-46 ng/L. Methyl Hg concentrations in the water column ranged from 0.27-5 ng/L from 1978-1980, with the highest values observed around Clay Lake (Parks et al., 1989)

The Ottawa River in Ontario, Canada has historically received substantial inputs of organic material from industrial and municipal sources, and has been used extensively for logging operations. This site also has shown contamination of Hg. The main source of Hg to the Ottawa River was the use of phenylmercuric acetate as a alimicide in pulp processing, before its use was discontinued in 1970 (Ottawa River Project Group, 1970) Studies conducted on the Hg concentrations in the river showed that the Hg_T concentrations have decreased significantly following the elimination of Hg inputs from

38 ng/L in 1972, 18 ng/L in 1973, 13 ng/L in 1975 –1976 to 6.6 ng/L 1978 (Kudo et al.,

1977; 1978 and 1982).

1.4 Mercury Contamination of Onondaga Lake

Onondaga Lake is a small, rapidly flushing lake located in metropolitan Syracuse,

New York. Although this lake was a major recreational resource to the region in the late

1890's and early 1900's (Lipe et al., 1983), fishing and contact recreation activities were

essentially eliminated as a result of degradation of the lake by domestic sewage and

industrial wastes. Much of the industrial pollution of the lake has been associated with

discharges from an adjoining chemical facility (Effler, 1987) that closed in 1986. Also,

the Onondaga County Metropolitan Syracuse Treatment Plant (METRO) discharges

treated domestic and industrial wastes directly into Onondaga Lake. Due to the plant's

design and size limitations, ammonia and phosphorus are discharged to the lake in

quantities that contribute to water quality problems (Onondaga Lake Management

Conference, 1993).

Despite reductions in the concentrations of various pollutants, Onondaga Lake

remains highly polluted and hypereutrophic. Continuing manifestations of the lake's

degraded condition associated with sewage discharges, include low transparency (Devan

and Effler, 1984), high standing crops of phytoplankton (Auer et al., 1990), extended

periods of hypolimnetic anoxia (Effler et al., 1988), severe lake-wide depletion of O_2

during fall turnover (Effler et al., 1988), and high concentrations of public health

indicator bacteria (fecal coliform) following run-off events (Auer et al., 1990).

A major water quality problem of Onondaga Lake is contamination by Hg. The adjoining chemical facility discharged large quantities of Hg waste to Onondaga Lake, between 1947 and 1970. Most of the waste emanated from two Hg-electrode cells used in chlorine production. It is estimated that approximately 75,000 kg of Hg were discharged by the facility into the lake from 1946 to 1970 (USEPA, 1973). The daily load from the facility was reduced from approximately 10 kg/day to less than 0.5 kg/day soon after the U.S. Department of Justice took legal action against the facility in 1970. The discharge was greatly decreased when the facility closed in 1986.

Onondaga Lake was closed to fishing in 1970 because of the excessive Hg contamination of fish tissue. The criterion used for the closure was the U.S. Food and Drug Administration (FDA) interim action level of 0.5 ppm in fish tissue. The action level was changed to 1.0 ppm in 1979 (NYSDEC, 1989). Onondaga Lake was reopened to recreational angling in 1986 on a 'catch and release' basis, but fish taken from the lake should not to be eaten, as a large fraction of the legal size fish continue to exceed the FDA criterion level (NYSDEC, 1987).

The New York State Department of Environmental Conservation initiated a yearly monitoring program for Hg in fish tissues in Onondaga Lake in 1970. At that time Hg concentrations averaged about .0 μg/g in 12 of 13 fish species (all sizes) studied, indicating that the fish of Onondaga Lake were well above the current FDA criterion (NYSDEC, 1987).

Decreases in fish tissue concentrations were reported through the 1970's, presumably in response to the reduction in loadings of Hg. In the early 1980's, however, Hg concentrations were observed to increase again after the adjoining chemical facility

closed in 1986 (Effler, 1987). Data from 1985 and 1986 samples show Hg concentrations in 10 species averaging below 1.0 µg/g, but legal-sized smallmouth bass, and walleye averaged above 1.0 µg/g. The proportion of smallmouth bass and walleye, of legal sizes, which exceeded 1.0 µg/g in 1985, were 81 % and 76 %, respectively. In 1986, the percentage of legal size smallmouth bass above 1.0 µg/g was 70 %. Concentrations of Hg in smallmouth bass (4 – 6 year age class) between 1975 and 1986 were relatively consistent (0.65-1.31 ppm). However, following closure of the chemical facility in 1986, a marked increase in fish Hg concentrations occurred (1.45-2.13 ppm). The concentrations subsequently decreased (0.72-1.36 ppm) in the early 1990s, and have remained constant at values similar to those occurring in the early 1970's. The reason for these long term patterns in fish Hg concentration is unclear.

Bloom and Effler (1990) conducted a preliminary study of Hg chemistry in the water column of Onondaga Lake. Concentrations of Hg_T were very high in Onondaga Lake, ranging from 7 to 26 ng/L (Effler et al., 1995). The reported concentrations of Hg, exceeded values reported for uncontaminated surface waters by about an order of magnitude. The lake contained elevated concentrations of CH_3Hg^+ (Bloom and Effler, 1990; Jacobs et al., 1995), the form that accumulates in fish tissue (Grieb et al., 1989). The concentrations of Hg reported in previous studies are summarized in Table 4. Concentrations of Hg_T were highest throughout the watercolumn in the spring. From spring to summer concentrations of Hg_T increased with increasing depth in the lake. Like Hg_T, concentrations CH_3Hg^+ increased with increasing depth (Effler et al. 1995). The highest concentrations of CH_3Hg^+ were observed in the lower waters during summer stratification.

Table 1.4 Concentrations of Hg in the water column, sediments and fish measured in previous studies of Onondaga Lake.

Media	Species	Jacobs Et al. (1995)	Wang and Driscoll (1995)	Bloom and Effler (1990)	Klein and Jacobs (1995)	NYS DEC (1987)
Epilimnion (ng/L)	Hg_T	3.0-9.4	4.0-15.7	7.1-18.8		
	CH_3Hg^+	0.2-1.0		0.4-2.0		
Hypolimnion (ng/L)	Hg_T	5.3-21.7	1.4-34.9	10.1-25.7		
	CH_3Hg^+	0.4-21.7		1.61-6.68		
Sediment (µg/g)	Hg_T				1.0-1.8	
Smallmouth bass (µg/g)	Hg					0.95-1.4

The fraction of Hg_T occurring as CH_3Hg^+ increased from about 11 % in the oxic upper waters to about 20 % in the anoxic waters (Effler et al., 1996). Bloom and Effler (1990) found that the volatile species Hg^0 made up small fraction of the total, with Hg^0, averaging about 0.6 % of the total. Concentrations of Hg^0 varied somewhat through the year, displaying the lowest concentration (> 0.05 ng/L) is the hypolimnion during periods of anoxia and reaching highest concentrations (from 0. to 0.5 ng/L) in near surface water in 1992 (Jacobs et al., 1995).

It has generally been thought that sediment contamination is the major source of Hg in fish tissue in Onondaga Lake. However, recent Hg data from sediment profiles (Jacobs and Klein, 1995; Rowell, 1996) and input waters (Bloom and Effler, 1990; Driscoll and Wang, 1996; Henry et al., 1995) suggest that continuing inputs from tributaries or precipitation, may also be an important component of continuing Hg contamination into the lake. Sediment data indicate that much of the Hg contamination has been buried by recent deposition (Rowell, 1996). According to Rowell (1996), the

increase in Hg concentration represents loadings no older than 1946 when release from the chlor-alkali facility was initiated. Between 1946 and 1970, concentrations of Hg in sediments ranged from 35 to 70 μg/g, while concentrations of Hg in sediments ranged < 10 μg/g after 1970 (Rowell, 1996) The top sediment samples (0 – 2.5 cm) from Onondaga Lake showed Hg concentrations of 1 to .8 μg/g, which is consistent with average Hg concentrations in sediments trap materials collected in the hypolimnion of the lake in 1992 (Klein and Jacobs, 1995). It is possible that the high Hg concentrations observed in the water column and the persistence of elevated concentrations of Hg in fish tissue, are largely results of continuing external loading

1.4.1 Previous Studies of Total Mercury and Methyl Mercury Fluxes in Onondaga Lake

Several studies have estimated Hg_T and CH_3Hg^+ loadings for input waters of Onondaga Lake (Table 1.4.1.A and .4 .B). The studies by Driscoll and Wang (1996) and Henry et al. (1995) were done during 1992, while Gbondo-Tugbawa et al. (1998) investigated Hg inputs to Onondaga Lake 1995. Mercury budgets from previous studies (Gbondo-Tugbawa and Driscoll, 1998; Driscoll and Wang 1996; Henry et al., 1995) showed that Ninemile Creek contributed high loads of Hg_T to the lake. Driscoll and Wang (1996) and Gbondo-Tugbawa and Driscoll (1998) indicated that about 43 % of the Hg_T load of Ninemile Creek was derived from the reach between Amboy and Lakeland, the site of the former chlor-alkali facility The Gbondo-Tugbawa et al 1998) indicated that both METRO (Onondaga County's Metropolitan Syracuse Treatment Plant) and Ninemile Creek contributed high inputs of Hg_T to Onondaga Lake The combined loadings of Hg_T for the major input waters including Ninemile Creek, Onondaga Creek,

Harbor Brook, Ley Creek and METRO obtained by Gbondo-Tugbawa et al. (1998) (10.5

kg/year) were intermediate between the values reported by Driscoll and Wang (1996)

(6.04 kg/year) and Henry et al. (1995) (13.15 kg/year). Of these mass balance studies,

the one conducted by Gbondo-Tugbawa et al (1998) is the most comprehensive because

samples were collected from all major tributaries and METRO throughout the year

(October 1995 to September 1996). In all the studies, Ninemile Creek had the highest

yield of Hg_T and the contribution of Hg_T loading from Ninemile Creek was more than

twice the combined contribution of the Harbor Brook, Ley Creek and Onondaga Creek.

Total loadings of CH_3Hg^+ for Ninemile Creek, Onondaga Creek, Harbor Brook.

Ley Creek and Metro, estimated by Gbondo-Tugbawa et al. (1998) (0.45 kg/year) were

higher than those reported by Henry et al. (1995) (0.26 kg/year). The loadings of

CH_3Hg^+ estimated in both studies (Gbondo-Tugbawa et al. 1998 and Henry et al., 1995)

showed that METRO was the highest contributor of external CH_3Hg^+ inputs to Onondaga

Lake. Henry et al. (1995), however, reported that the loading of CH_3Hg^+ from METRO

was 58% of the total load from the input waters, and this is higher than the value

estimated in Gbonda-Tugbawa et al 1998) (44%).

Table 1.4.1.A Summary of Hg_T loadings (kg/year) for input waters of Onondaga Lake reported in previous studies.

	Gbondo-Tugbawa et al. (1998)	Driscoll and Wang (1996)	Henry et al. (1995)
Harbor Brook	0.067	0.040	0.220
Ley Creek	0.282	0.220	0.409
Onondaga Creek	1.422	0.760	1.811
Ninemile Creek	4.408	3.500	7.094
Metro	4.319	1.520	3.620
Total			

Table 1.4.1.B Summary of CH₃Hg⁺ loadings (kg/year) for input waters of Onondaga Lake reported in previous studies.

	Gbondo-Tugbawa et al (1997)	Henry et al. (1995)
Harbor Brook	0.0075	0.0087
Ley Creek	0.0193	0.0052
Onondaga Creek	0.0857	0.0492
Ninemile Creek	0.1458	0.0478
Metro	0.1906	0.151
Total	0.4489	0.2619

The differences in Hg loadings may be due to differences in discharges, concentrations of Hg species, the period of study and/or method of flux estimation. In addition, differences in the patterns of monthly Hg concentrations and daily discharges may be also be responsible, since the product of both quantities were considered in loading calculations.

The rates of Hg_T and CH_3Hg^+ accumulation in the hypolimnion of Onondaga Lake during summer stratification were estimated by Gbondo-Tugbawa and Driscoll (1998). The internal rate of Hg_T release in the hypolimnion was .97 kg/year. This value is higher than the rate estimated by Driscoll and Wang, 1996   .2 kg/year). The rate of CH_3Hg^+ release was 1.0 kg/year was about half the estimated rate of Hg_T release.

The sinks of Hg_T and CH_3Hg^+ include outflow, volatilization and sediment burial. Outflow of Hg_T was estimated by Driscoll and Wang, 1996 (5.6 kg/year) and Henry et al., 1995 (2.8 kg/year). Henry et al. (1995) also estimated an outflow of CH_3Hg^+ (0.24 kg/year). Volatilization value of Hg_T was estimated by Bloom et al., 1989 (0.15 kg/year) and Henry et al., 1995 (0.016 kg/year). Sediment burial of Hg_T was estimated by Henry

et al., 1995 (11.24 kg/year), while Henry et al. (1995) estimated sediment burial of CH_3Hg^+ (0.60 kg/year).

Differences in fluxes could be due to the method of flux estimation. However, inputs from the tributaries were the major external source of Hg_T to the lake in all studies. While Driscoll and Wang (1996) indicate that outflow was the major sink of Hg_T, Henry et al. (1995) reported that net sedimentation was the major sink. For CH_3Hg^+, net methylation was the major source (Henry et al., 1995) (0.63 kg/year) and sediment burial was the major sink (Henry et al., 1995) (0.60 kg/year).

1.4.2 Applications of Mercury Cycling Models to Onondaga Lake

The Onondaga Lake Mercury Model (OLMM) was also developed to simulate Hg cycling in Onondaga Lake. The model calculates the concentrations of Hg_T, CH_3Hg^+, Hg^0 and Hg^{2+} in both dissolved and particulate forms in the water column. The model was calibrated to an extensive data set of temporally and spatially variable Hg concentrations in Onondaga lake in 1992 (Henry et al., 1995). The OLMM includes remineralization to simulate release of Hg from settling particles before incorporation into sediment. The model provides an analytical framework for understanding and predicting the behavior of Hg in Onondaga Lake and potential use in evaluating the relative impact of different source control and remedial alternatives.

Recent, Gbondo-Tugbawa and Driscoll 998) conducted a preliminary calibration of the Regional Mercury Cycling Model (R-MCM) to Onondaga Lake. They were able to effectively calibrate the model based on a limited data set. Model predictions of water column Hg_T and CH_3Hg^+ and fish Hg concentrations suggest that these values are very responsive to decreases in external inputs of Hg_T.

Although there have been several studies of the biogeochemistry Hg of Onondaga Lake, there has been little efforts directed at compiling, integrating and synthesizing this information. With a compilation of Hg data for Onondaga Lake, this provides an opportunity to recalibrate the R-MCM and conduct a more detailed assessment with this research and management tool.

1.5 Study Objectives

The objective of this study was to better understand the processes regulating of the concentrations of Hg species in the water column, sediments and fish of Onondaga Lake. The specific objectives were: (1) to provide a synthesis of patterns of Hg_T and CH_3Hg^+ concentrations and transfers in the water column, sediments and fish of the lake. (2) to use the Regional Mercury Cycling Model (R-MCM) to simulate mass fluxes of Hg_T and CH_3Hg^+ in the lake, and (3) using this model predict the concentrations of Hg species in the water column, sediments and fish of the lake under different scenarios such as external Hg loads and changes in lake chemical characteristics to better understand how the biochemistry of Hg in the lake might respond to management scenarios.

Chapter 2 - Study Area

2.1. Location and Morphometry

Onondaga Lake is located (43°06'54"N; 76°14'34"W) immediately north of the City of Syracuse, in Onondaga County, New York (Figure 2.1.A). Onondaga Lake is in the Oswego River drainage basin (Figure 2.1.A, inset). The outflow from the lake exits through a single outlet at its northern end and enters the Seneca River. The Seneca River combines with the Oneida River to form the Oswego River, which flows north, entering Lake Ontario at Oswego (Figure 2.1.A).

The lake covers an area of 12×10^6 m², has a volume of 131×10^6 m³, a mean depth of 10.9 m and a maximum depth of 19.5 m. The lake is oriented along a northwest-southeast axis (Figure 2. .B). It has a length along this axis of 7.6 km and a maximum width of 2 km. The lake is commonly described as having two basins, the south and north, that are separated by a modest "saddle" region that is located approximately 3.6 km from the outlet. Tributaries to Onondaga Lake flush the lake rapidly compared to many other lakes in the region, approximately four times each year (Onondaga Lake Management Conference. 1993; Effler and Harnett, 1996).

2.2. Climate

The climate of the Onondaga Lake drainage basin can best be described as humid, continental. Most of the precipitation is the result of cyclonic storms derived from the Great Lakes basin in the interior of the North American continent (Ruffner and Blair, 1987). The climate is strongly influenced by geographic differences between the Ontario
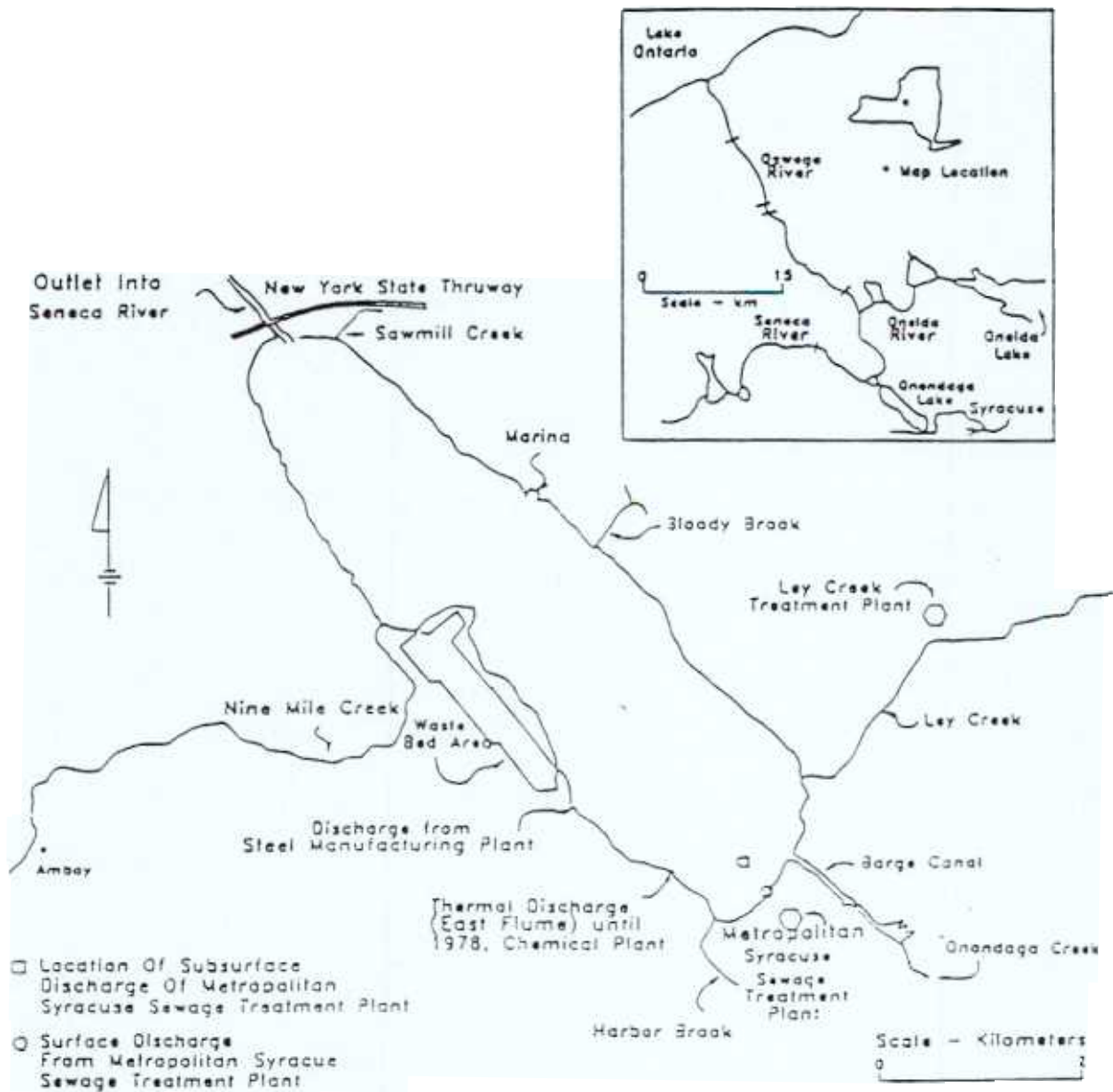
Figure 2.1.A Onondaga Lake, showing the input waters (after Effler, 1996)

Bathymetric Map of

Onondaga Lake

Onondaga County, New York

Contours in meters

Based on survey of June, 1987

level gauge

N

Scale in kilometers

Sampling Stations:
S — south, primary
N — north
SA — saddle

Metropolitan
Treatment Plant
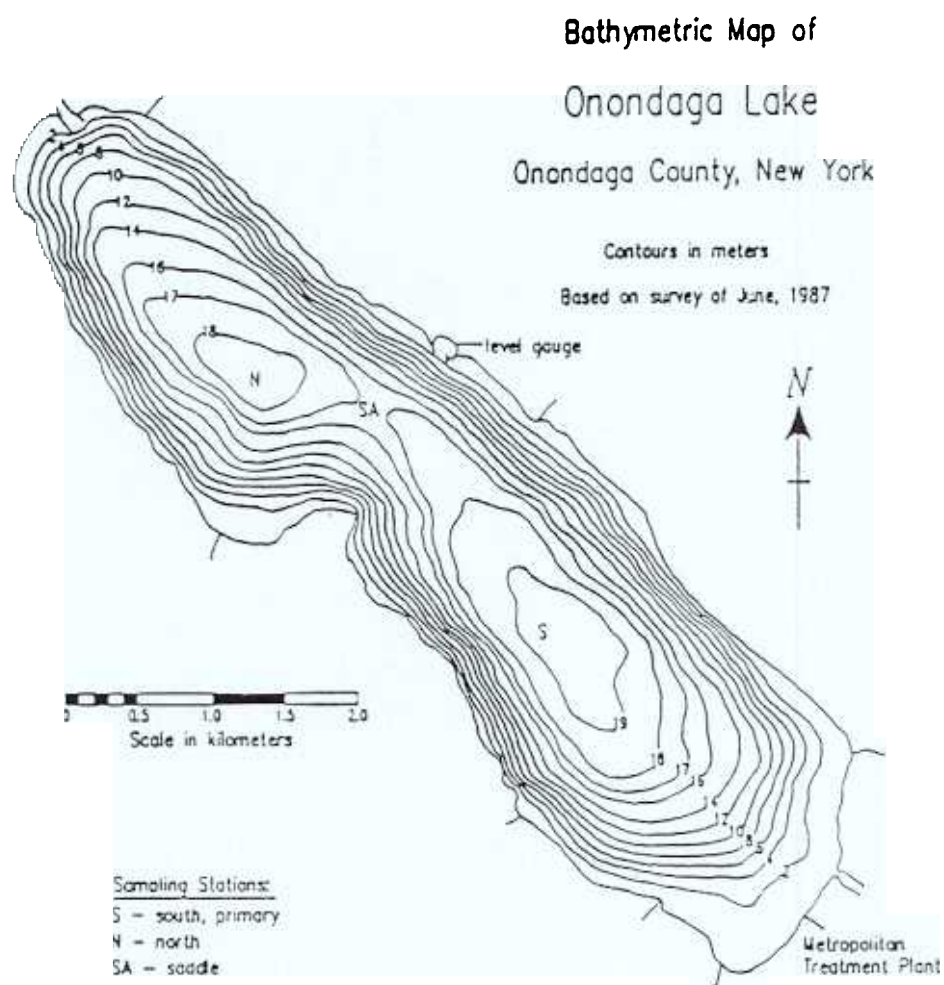
**Figure 2.1.B Bathymetric map of Onondaga Lake, based on 1987 soundings
(after Owens, 1987)**

Lowlands of the northern portion of the drainage basin and the Appalachian Upland to the south (Effler and Harnett, 1996).

Lake Ontario influences the local weather by moderating air temperatures and reducing extremes in both hot and cold temperature. The average daily high temperature for Syracuse in July is 27.7°C, with an average January low temperature of –9.4°C (Ruffner and Blair, 1987). The proximity of Lake Ontario also results in considerable cloudiness, especially during the winter months. Cold air from the west and northwest often moves across the large, unfrozen surface of Lake Ontario acquiring moisture. This creates "lake-effect" snow squalls and storms during the mid-October to mid-March period (Winkley, 1989). Rather localized differences in annual snowfall are evident, with the highest average annual totals of 254 to 305 cm occurring in the northern and eastern parts of Onondaga County (Hutton and Rice 1977). Precipitation in the Onondaga Lake drainage area is generally evenly distributed, with the summer months being the driest on average.

2.3. Tributaries and Subbasins

The major natural tributaries to Onondaga Lake are Ninemile Creek and Onondaga Creek which together account for about 62% of the total amount of water that flows into the lake each year (Effler and Whitehead, 1995). Other natural tributaries to the lake are Ley Creek, Harbor Brook and Bloody Brook. The Metropolitan Syracuse Treatment Plant (METRO) of Onondaga County is the third largest source of water to the lake, making up 18% of the annual inflow. This large proportion of treated wastewater is a unique feature of Onondaga Lake and a leading source of its continuing water quality

problems. During the summer, when the amount of water flowing into the lake from the natural tributaries is low, the discharge from METRO represents a much larger contribution of water to Onondaga Lake (Effler and Whitehead, 1995). Other minor tributaries include Sawmill Creek, Tributary 5A, and the East Flume (Figure 2.1). The Onondaga Lake watershed is approximately 642 km^2 and lies entirely within Onondaga County, with the exception of a small portion (about 2 km^2) that lies in north central Cortland County (Effler and Harnett, 1996).

Ninemile Creek discharges into Onondaga Lake on its western shore; its watershed drains approximately 298 km^2 both south and west of Onondaga Lake. The Ninemile Creek watershed originates at the outlet of Otisco Lake. The total length of the Ninemile Creek mainstream is 55.2 km.

Onondaga Creek drains an area of approximately 298 km^2 and has a mainstream length of approximately 44.2 km. The Tully mud boils, a major source of sediment to the creek and lake (Effler et al. 1992), are located about 33 km above the creek mouth. Onondaga Lake empties into the southern end of Onondaga Lake. The lower reaches of the creek drain a significant portion of the City of Syracuse.

The Ley Creek watershed is approximately 77.4 km^2, extending eastward from the southern end of Onondaga Lake. This lake watershed is residential and industrial in character, with the exception of the headwaters that are located primarily in wetlands. This watershed has become increasingly developed in recent decades.

Harbor Brook extends to the southwest from its mouth on the southernmost end of Onondaga Lake. It has a long and narrow watershed of approximately 29.3 km^2. The lower reach drains a portion of the City of Syracuse, while the headwaters drain a mixture

of residential, agricultural, and pasture lands. This area has become more residential during the last decade.

Bloody Brook enters Onondaga Lake at roughly the midpoint of its eastern shore in Onondaga Lake Park. The watershed of approximately 29.3 km^2 extends to the northeast draining the lake plain area, which is heavily residential

2.4 Waste Sources

Onondaga Lake has been the principal receptacle for wastes from the Syracuse area from the early development of the region to the present. The most clearly manifested and pervasive industrial impacts have been associated with a chemical manufacturing facility (soda ash and other products) on the west shore (Effler, 1987)

2.4.1 Allied Signal

The chemical plant on the western shore of Onondaga Lake has had a major environmental impact on the Syracuse area. The plant was originally built to produce sodium carbonate (Na_2CO_3), commonly referred to as soda ash. Soda ash is used in softening water and in the manufacture of glass, soap, and paper. The chemical facility was situated in an ideal location because of the local abundance of the raw materials and ample opportunity to dispose of associated wastes. More than 30 chemicals were manufactured at the plant over its 102 years tenure (Effler and Harnett, 1995) Two of the most important processes that have impacted the lake are the production of soda ash, and 2) Cl_2 and NaOH (chlor-alkali process)

A. Soda Ash

The production of large quantities of waste accompanied the soda ash manufacturing process. A waste slurry containing $CaCl_2$, excess CaO, unreacted $CaCO_3$ and NaCl, $CaSO_4$, and lime impurities, was pumped to waste beds where the soluble fraction (waste bed overflow) drained off and entered the lake (mostly via Ninemile Creek since the early 1940s). The waste bed overflow was enriched in Cl^-, Na^+, and Ca^{2+}. According to Effler (1987), average daily load of the ionic waste to the lake between 1971 and 1981 was approximately 2.5×10^6 kg/day.

The salinity characteristics of Onondaga Lake were reviewed for the late 1960s to 1990 interval. The dominant anion has been Cl^-; the dominant cations have been Ca^{2+} and Na^+. This composition largely reflects the high loads of these materials received as waste from soda ash production (Effler and Whitehead, 1996).

B. The Chlor-Alkali Process

The availability of salt also promoted the establishment of a chlor-alkali process at the Allied facility. In the chlor-alkali industry, the major process is electrolysis of aqueous NaCl solution to produce NaOH and chlorine. The aqueous chloride ion is oxidized at a carbon anode by the reaction $2Cl^- \rightarrow Cl_{2(g)} + 2e^-$ while water is reduced at a Hg or carbon cathode:

$$2e^- + 2Na^+ + 2H_2O \rightarrow 2Na^+OH^- + H_{2(g)}$$
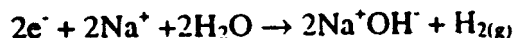
Mercury cells are not the only types of cells possible for this process, but they were widely used when facilities were developed earlier this century. The NaOH product, the spent NaCl solutions and other plant effluents carry traces of Hg into the discharge tubes and from there to receiving waters

Ideally Hg should be recirculated in the process and not released to the environment. However, typically there are losses to leakage and discharge, as the cells are cleaned or replaced.

2.4.2 Domestic Waste

From the early twentieth century, Onondaga Lake received increasing amount of untreated domestic waste via the tributaries of Onondaga Creek, Harbor Brook, and Ley Creek. In 1922 the interceptor sewer system consisting of two sewers paralleling Onondaga Creek and Harbor Brook was completed. A primary sewer treatment facility was constructed in 1925 adjoining the southern shore to serve the interceptor system, which carried 90% of the city's sewage (Effler, 1996). With the growth of the city of Syracuse, the Ley Creek Sewage Treatment Plant was built in 1934. This secondary treatment (activated sludge) facility was expanded to an average capacity of 9 million gallon per day (MGD). An additional   MGD primary treatment capacity was added in 1950 because of the increasing industrial load. However, this facility became overloaded soon after.

In 1960 Onondaga County completed construction of a primary treatment plant (METRO) on the southeastern shore of the lake. METRO was designed to treat 50 MGD of sewage. It could accommodate a peak flow of 170 MGD. Flow in excess of this quantity was bypassed directly to the lake following screening. Major upgrades to METRO were made in the late 1970s (secondary treatment) and early 1980s (tertiary treatment; phosphorus removal). This facility was designed to treat an average flow of 80 MGD; flows up to 120 MGD receive full treatment. Peak flows of 223 MGD can be accommodated. Flows in excess of 120 MGD receive incomplete treatment (primary

treatment and chlorination). The layout of the METRO facility is presented in Figure 2.4.2.

Interceptor sewers of the early 1900s were the combined type, intended to carry both sanitary and stormwater flows (combined sewage); thus, the evolution of the 66 combined sewer overflows (CSO) system that exist today. During heavy rain storms, excess flow from the sewer system never reaches the METRO plant, and untreated diluted sewage and floating debris are discharged to the tributaries of Onondaga Lake.

2.5   Pollution Problems

A. Salinity (pH, Ca^{2+}, $CaCO_{3(S)}$ and inorganic carbon)

Onondaga Lake is characterized by hard water (Effler and Driscoll, 1985). The concentrations of four major cations, Ca^{2+}, Mg^{2+}, Na^+, K^+, and three major anions, HCO_3^-, SO_4^{2-} and Cl^-, essentially constitute the total ionic salinity of most fresh waters, as other ions make very minor contributions (Wetzel, 1983). In Onondaga Lake, the dominant anion has been Cl^-; the dominant cations have been Ca^{2+} and Na^+. This composition largely reflects the high loads of these materials received as water from soda ash production (Effler et al., 1996). The contribution of these three constituents to the salinity of the lake has decreased since the closure of the chemical facility in 1986. The contribution of these three constituents to the salinity of the lake has decreased since the closure of the soda ash/chlor-alkali facility from more than 85% to 70%. The Cl^- level in the lake has decreased approximately 70% since closure of the facility (Effler, 1987). Thus, Cl^- represented about 55% of salinity before closure; now it is about 40% (Effler and Whitehead, 1996).
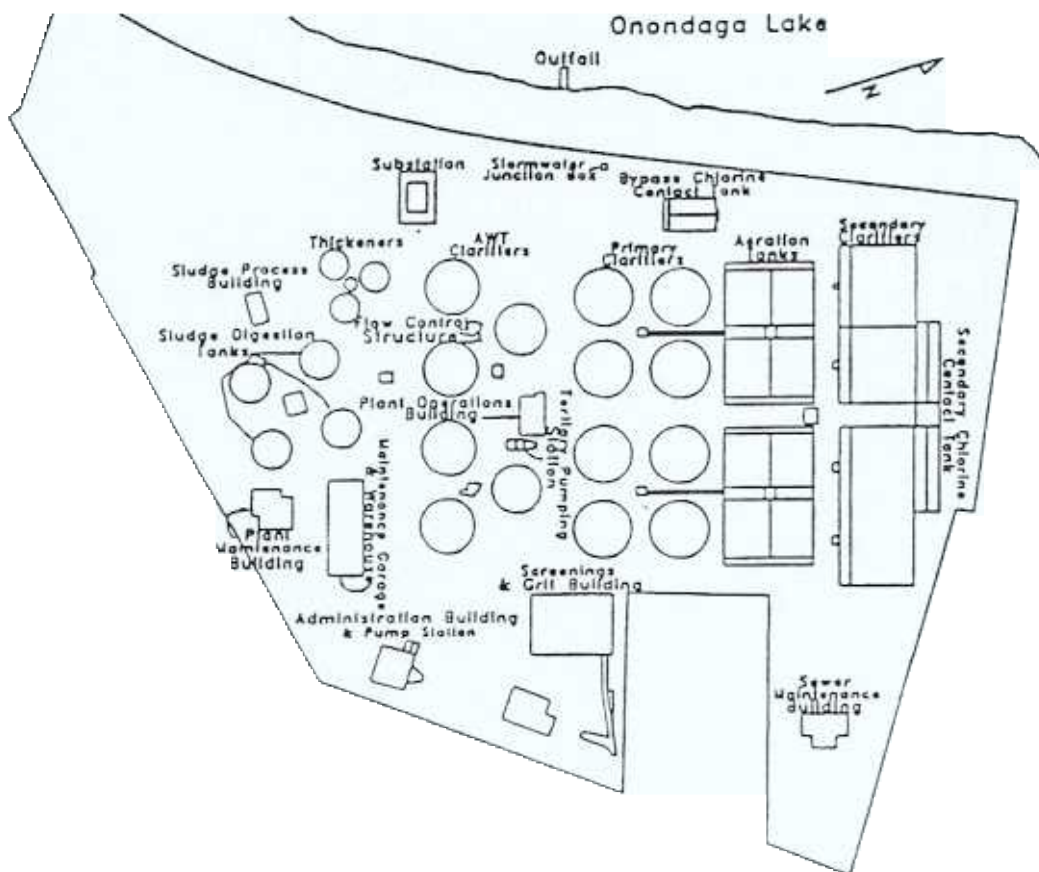
Figure 2.4.2 Layout of the Syracuse Metropolitan Wastewater Treatment Plant (METRO) (after Effler, 1996)

The elevated salinity of Onondaga Lake undoubtedly reduced the diversity of its aquatic life (Auer et al., 1995). High concentrations of calcium discharged to the lake from soda ash production has resulted in the precipitation of large quantities of calcium carbonate which has accumulated on in lake sediments. These deposits have accelerated the rate at which Onondaga Lake is filling in and eliminated habitats that support near-shore biological communities. Because high ionic strength water is denser than fresh water, high salt loadings also altered the natural stratification cycle of Onondaga Lake, although this distribution has been greatly reduced since the closure of the soda ash facility. The Seneca River, a moving body water that should not stratify through the year, also experiences chemical stratification as a result of receiving denser, saline water from Onondaga Lake (Owens and Effler, 1995).

The lake water is well buffered, with pH values between 7 to 8.5 (Effler, 1987a: Driscoll et al., 1993). Peak pH values are observed in the near surface waters of Onondaga Lake during phytoplankton blooms and pH decline with increasing depth coinciding with increased production of CO_2 in the lower waters

The lake becomes oversaturated with respect to the solubility of $CaCO_3$ (calcite) during the productive summer period, as a result of increased temperature (Brunskill, 1969; Strong and Eadie, 1978) and the photosynthetic process (Effler 1984; Effler and Driscoll, 1985; Effler et al., 1981, 1982; Otsuki and Wetzel, 1974). The precipitation and deposition of $CaCO_3$ results in the removal of aqueous Ca^{2+} and dissolved inorganic carbon, and often the accumulation of $CaCO_3$ in underlying sediments (Jones and Bowser, 1978). This process may influence the cycling of constituents such as P (Otsuki and Wetzel, 1972; Murphy et al. 1983; Wodka et al., 1985), and other particles that serve

as nuclei for precipitation (Johnson et al. 1991). Further, water clarity may decrease greatly during periods of CaCO₃ precipitation due to increase in light scattering (Effler et al., 1987; Effler et al., 1991; Weidemann et al., 1985). The average rate of CaCO₃ deposition during summer decreased from about 0.196 to 0.082 mol/m²-day following the closure of industrial source of Ca^{2+} pollution. However, the extent of oversaturation with respect to calcite solubility remains essentially unchanged.

B. Phosphorus

Phosphorus is an element that is important to plant nutrition. The amount of phosphorus in the lake is an important factor to determine water quality, because phosphorus stimulates the growth of algae. High phosphorus loading causes excessive growth of algae in Onondaga Lake during most of the summer. The algae give the water a cloudy, green appearance and decrease the clarity of the lake. After the algae die and settle to the lower water, the decomposition of this organic detritus results in the depletion of oxygen in the hypolimnion (Effler et al., 1995).

C. Dissolved Oxygen

The oxygen resources of Onondaga Lake are extremely limited because the lake is highly eutrophic. Dissolved oxygen (DO) is depleted rapidly from the hypolimnion soon after the onset of density stratification. The DO decreases with increasing depth, during summer stratification, reflecting the localization of oxygen demand at the sediment-water interface and limited vertical mixing in the hypolimnion (Effler et al., 1996).

The by-products of the decomposition of algal detritus such as hydrogen sulfide, methane and ammonia accumulate in the lower lake waters following the loss of oxygen (Effler et al., 1995). Hydrogen sulfide accumulates to very high concentrations   55

mmol/L) during summer stratification due to high natural inputs of SO_4^{2-} coupled with elevated deposition of organic matter to the hypolimnion (Effler et al., 1988). Concentrations of H_2S observed in Onondaga Lake are among the highest values reported in the literature for fresh water (Effler et al., 1995). The severe DO depletion causes anaerobic conditions to develop in the hypolimnion. The high rates of organic matter deposition facilitate the depletion of DO in the lake. The accumulation of reduced species in the hypolimnion during summer stratification is oxidized during fall turnover, resulting in the lowest concentrations of DO throughout the water column during the period.

D. Mercury

Onondaga Lake contains high concentrations of Hg in its water column (Bloom and Effler, 1990), sediment (NYSDEC, 1990) and fish tissue. See chapter 1 for more details.

2.6   Plants and Animals

The biotic community (plants and animals) are critical to the function of the Onondaga Lake ecosystem. Their life processes are ultimately powered by the sun converting energy from one form into another. Each organism has a function that is completely codependent on interactions with other organisms within the lake. These interactions are referred to as a food web (Figure 2.6).

Much of the plant life in the open waters of Onondaga Lake is microscopic and drifts with the movement of the water. The food web in the open water consists of algae,

Nutrient Sources

**POINT SOURCES
NON-POINT SOURCES
LAKE RECYCLING** → Nutrients
Phosphorus and Nitrogen

Algae

Predator Fish
(walleye)

Zooplankton
(Daphnia)

Small Fish
(young yellow perch)
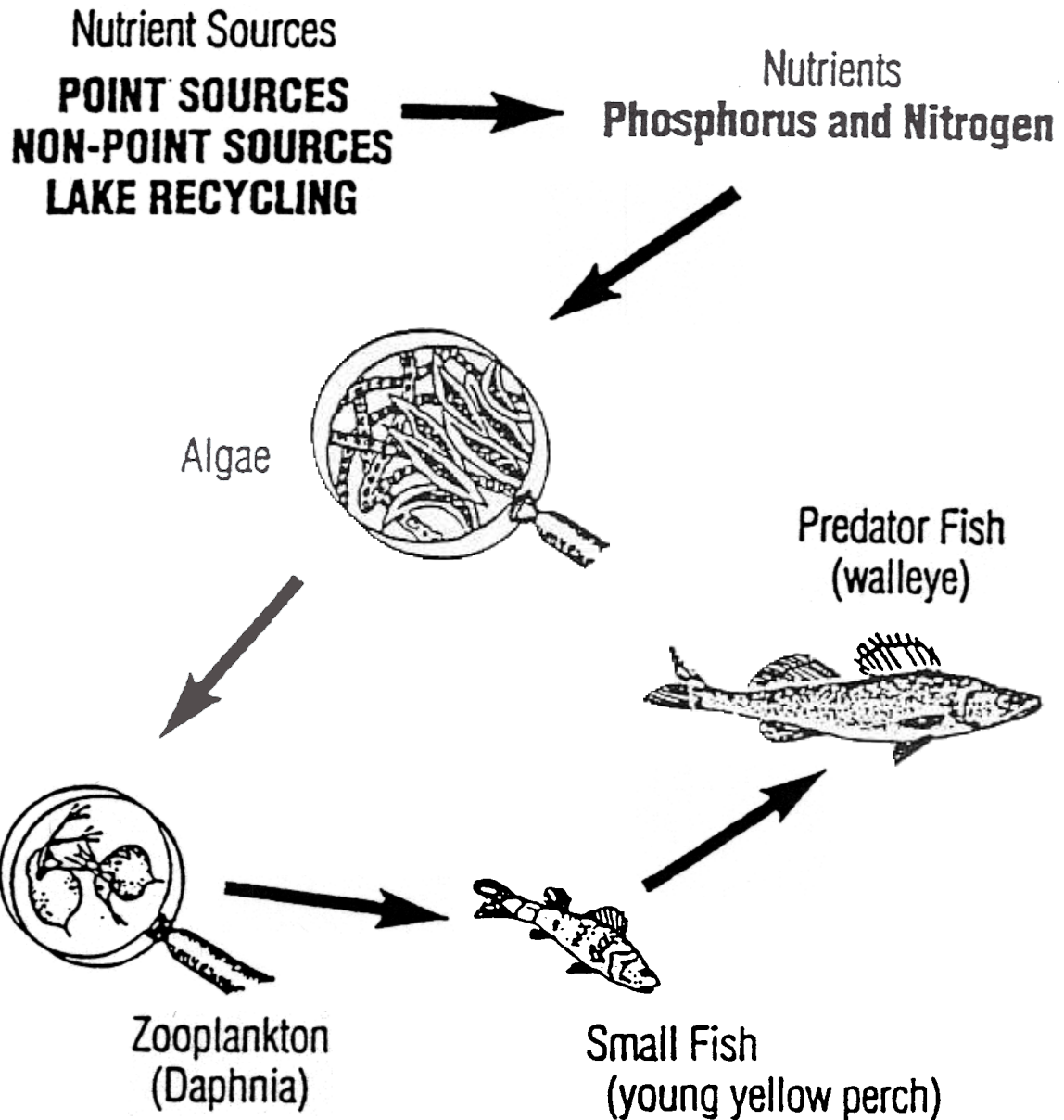
Figure 2.6 A typical food web of a temperate lake ecosystem
(after Onondaga lake Management Conference, 1993)

zooplankton, macroinvertebrates and fish. Bacteria and fungi also thrive in the open water area.

Through ingestion, zooplankton are important in regulating algae concentrations in many lakes. Algae, zooplankton and organic detritus that sink to the bottom of the lake are decomposed by bacteria and fungi living in the deep water. Bacteria and fungi largely mediate the decomposition of the organic matter releasing key nutrients such as phosphorus and nitrogen to the overlying water.

Invertebrates, such as worms and insect larvae, and also important in the consumption of organic detritus in many lakes. Examination of the deep-water sediments of Onondaga Lake has shown low populations of macroinvertebrates. This pattern may be consistent with low concentrations of dissolved oxygen and high concentrations of toxic materials in the deep-water areas (Auer et al., 1995).

2.7 The Lake's Fishery

Recent sampling efforts have identified a total of 52 different fish species in the Onondaga Lake (Auer et al., 1995). The species present include desirable sport fish such as largemouth and smallmouth bass, walleye and northern pike. Larger populations of golden shiner, white perch, gizzard shad, bluegills and pumpkinseed sunfish can also be found near the shoreline of the lake. The increasing populations and varieties of fish reflect a vast improvement from conditions in the 1950s when fishery surveys showed that more than 90% of the total fish in Onondaga Lake were common carp.

The Onondaga Lake fishery is currently made up of both year-round residents and transients that migrate in and out of the lake depending on changes in lakewide oxygen

levels. During fall turnover, for example, fish like smallmouth bass and walleye swim out of the lake outlet into the Seneca River in order to survive these low oxygen periods (Auer et al., 1995).

Diet information represents an important tool in evaluating the effects of perturbations in aquatic communities (Ringler, 1979 and 1990). The planktivorous fish community of Onondaga Lake is presently dominated by gizzard shad and white perch, particularly when young (Auer et al., 1995). Gizzard shad larvae feed on zooplankton. Adults gizzard shad are primarily phytophagous (Kutkuhn, 1957; Bodola, 1966; Tisa and Ney, 1991), and would be expected to demonstrate little size selective effects on the zooplankton. Benthivorous blue gill feed on benthic invertebrates and detritus (Auer et al., 1995). Omnivorous white perch can be planktivorous when they are young. White perch are found to feed on the eggs of fish (http://www.seagrant.wisc.edu). Smallmouth bass are piscivorous. Juveniles feed on aquatic insects. As they grow larger, older age-class prey on small fish (http://www.pvisuals.com).

Chapter 3 – Modeling Approach and Databases

3.1 The Regional Mercury Cycling Model (R-MCM), (Tetra Tech Inc, 1996).

The Regional Mercury Cycling Model (R-MCM) is a steady-state mechanistic simulation model which is used to study the biogeochemistry of Hg in lake/watershed ecosystems. Using a mass balance approach, the model predicts concentrations for three forms of Hg in six abiotic compartments and five trophic levels. Since the model is steady-state, inputs are fixed values and do not vary with time. The outputs are representative of conditions once a lake has stabilized to the input conditions provided.

There are three primary Hg forms in the model: CH_3Hg^+, Hg_T^{2+} and Hg^0. Mercuric ion is considered to consist of all Hg, which is neither CH_3Hg^+ nor Hg^0. Total Hg is calculated as the sum of CH_3Hg^+, Hg_T^{2+} and Hg^0. There is often reference in the literature to "reactive" Hg. This fraction of Hg_T^{2+} is operationally defined. In the model however, all Hg in the lake system is assumed to be available to participate in the Hg cycle (i.e., there is no "inert mercury'

Model compartments include the water column, sediments and a food chain that includes prey and predatory fish (Table 3.   Mercury concentrations in the atmosphere are used to calculate fluxes across the air/water interface (gaseous, wet deposition, dry deposition). Atmospheric conditions are defined by the user, rather than modeled.

The food chain consists of five trophic levels (phytoplankton, zooplankton, benthos, prey fish and predatory fish). Fish Hg concentrations tend to increase with age, and are therefore followed in each year class (up to 20 cohorts for prey and 15 for predators).

Table 3.1.1 Environmental compartments and mercury forms included in R-MCM model

Compartment	Mercury form			
	CH_3Hg^+	Hg_T^{2+}	Hg^0	Solid HgS
Water Column (abiotic)				
Dissolved	X	X	X	
Non-living suspended particles	X	X		X
Sediments				
Sediment Porewater	X	X	X	
Sediment Solids	X	X		X
Food Chain				
Phytoplankton	X	X		
Zooplankton	X	X		
Benthos	X	X		
Prey Fish Cohorts (15 max)	X			
Predatory Fish Cohorts (25 max)	X			

Total mercury is calculated as the sum of the individual Hg forms.
(Tetra Tech Inc., 1996)

3.1.1 R-MCM Processes

An overview of the major processes involved in the Hg cycle in lakes is shown in Figure 3. 1 These processes include inflows and outflows (surface and groundwater), adsorption/desorption, particulate settling, resuspension and burial, atmospheric deposition, air/water gaseous exchange, point sources of Hg, in-situ transformations (e.g. methylation, demethylation, Hg_T reduction), Hg uptake in plankton and zooplankton, and bioenergetics related to CH_3Hg^+ fluxes in fish. Because mechanistic models simulate the major processes occurring in a system, they can be used to investigate cause/effect relationships. They can also be used to develop and test hypotheses, scope field studies, and identify key research needs.

A. The Hg_T^{2+} Cycle

In the water column (epilimnion and hypolimnion) and sediments, the dissolved phase and non-living particles are assumed to be in equilibrium (rapid adsorption and
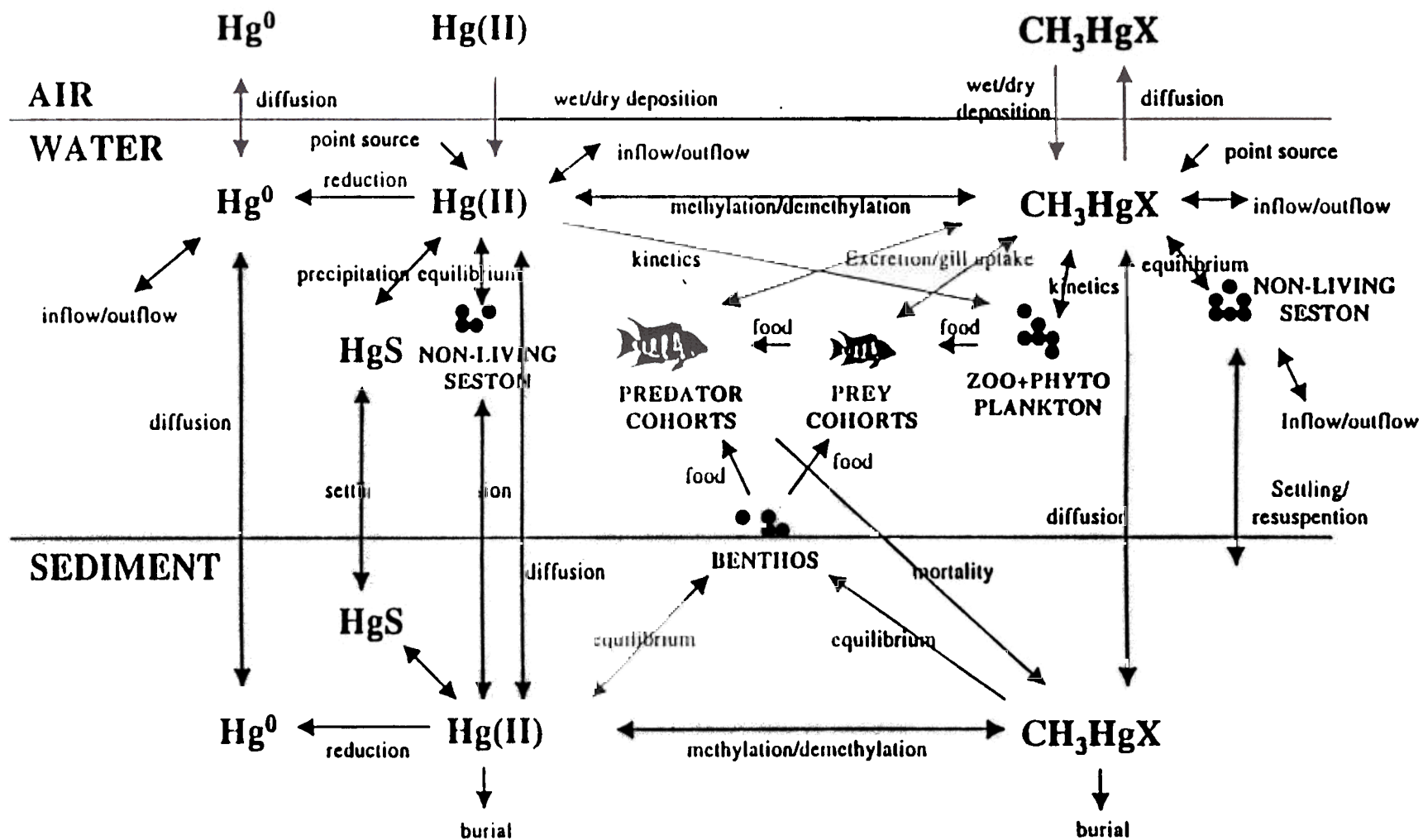
Figure 3.1.1 Representation of Hg Cycle in R-MCM Model (after Tetra Tech Inc.)

desorption) with either the free ion (Hg^{2+}) or complexes of Hg_T^{2+} associated with inorganic ligands (non-DOC bound).

Inorganic Hg (Hg_T^{2+}) can also form solid phase HgS under the appropriate anaerobic conditions. Solid phase HgS in the water column is assumed to be deposited in sediments. Partitioning of Hg_T^{2+} into phytoplankton is assumed to operate kinetically, not having time to reach equilibrium. Uptake of Hg_T^{2+} into phytoplankton is assumed to occur both passively and actively. Uptake is balanced by cell growth, division and depuration. It is recognized that zooplankton are not at true "equilibrium" with the dissolved phase, but for the purpose of the model, a simple partition constant is used to estimate zooplankton concentrations of Hg_T^{2+} on the basis of phytoplankton Hg_T^{2+} concentrations.

Other Hg_T^{2+} processes include inflows, outflows (surface and/or groundwater), settling of non-living particles into epilimnetic sediments and through the thermocline, Hg_T^{2+} diffusion across the thermocline and across the sediment/epilimnion interface, atmospheric deposition, Hg_T^{3+} reduction and methylation, and point sources of Hg_T^{2+}.

B. The CH_3Hg^+ Cycle

In the water column (epilimnion and hypolimnion) and sediments, the dissolved phase and non-living particles are assumed to be in equilibrium in terms of rapid adsorption and desorption of either CH_3Hg^+ or complexes of CH_3Hg^+ associated with inorganic ligands. Partitioning of CH_3Hg^+ into phytoplankton is assumed to operate kinetically, not having time to reach equilibrium. Uptake of CH_3Hg^+ into phytoplankton is assumed to occur both passively and actively. Uptake is balanced by cell growth, division and depuration.

Although zooplankton are not at true "equilibrium" with respect to CH_3Hg^+ in the dissolved phase, a simple partition constant is used to estimate zooplankton concentrations of CH_3Hg^+ on the basis of concentrations of CH_3Hg^+ in phytoplankton for the purpose of this model.

Kinetic CH_3Hg^+ processes include inflows, outflows (surface and/or groundwater), settling of non-living particles into epilimnetic sediments and through the thermocline, diffusion of CH_3Hg^+ across the thermocline and across the sediment/epilimnion interface, epilmnetic sediment resuspension, atmospheric deposition, volatilization, methylation, demethylation, and point sources of CH_3Hg^+.

C. The Elemental Mercury Cycle

Elemental Hg (Hg^0) is included in the model only in the dissolved form, and therefore is not subject to fluxes associated with particulate and the food chain. In the water column (epilimnion and hypolimnion), processes include inflow, outflow (surface and/or groundwater), Hg^0 diffusion across the thermocline and across the sediment/water interface, volatilization, Hg_T^{2+} reduction to Hg^0, and demethylation. Elemental Hg processes in sediments include Hg_T^{2+} diffusion across the sediment/water column interface and demethylation. Reduction of Hg_T^{2+} to Hg^0 is not included in sediments.

Elemental Hg concentrations are usually a small fraction of Hg_T in the water column. Elemental Hg is included in the model primarily for two reasons. First, volatilization of Hg^0 can be a significant flux of the Hg_T budget. Second, predicted concentrations of Hg^0 serve as a check on the rates associated demethylation and Hg_T^{2+} reduction.

D. Specific Mercury Processes

Methyl Hg and Hg_T^{2+} enter a lake directly by both wet and dry atmospheric deposition. Since this is a steady-state model, rates for these processes are constant in the simulations, and do not reflect seasonal changes or the effects of ice cover.

Three types of lakes can be considered: drainage lakes with surface inflows and outflows, groundwater-fed seepage lakes, and mounded seepage lakes which obtain their water inputs from direct precipitation only. Drainage lakes are assumed to receive their terrestrial Hg loads via surface inflows to the epilimnion. The path of the outflow depends on the lake type selected by the user when setting up the initial conditions in the lake. For drainage lakes, the outflow exits from the surface of the epilimnion. Surface outflows include dissolved and particulate Hg in seston.

Non-living particulates are allowed to settle in the model. Living plankton are assumed not to settle. Epilimnetic particles can settle either to epilimnetic sediments or through the thermocline into the hypolimnion. Hypolimnetic particles settle into hypolimnetic sediments. Elemental Hg is not included in the particulate fractions in the model. Sediment burial/erosion is incorporated into the model. These processes operate separately in the epilimnion and hypolimnion. For example, erosion can occur in the epilimnion, while burial occurs in the hypolimnion

Resuspension rates for sediment particles are calculated separately for the epilimnion and hypolimnion. Resuspension rates are difficult to estimate in the field and are therefore estimated by using a mass balance of sediments. The model includes four particulate fluxes in sediments. Three of the fluxes (settling velocity of particles in the water column, sediment burial rates and particle degradation rates to gaseous decomposition products) can be determined from field measurements. The single

unknown is the resuspension velocity, which is calculated to maintain the sediment mass balance.

Methylation is temperature dependent and assumed to be first-order with respect to organic carbon concentrations. This is in contrast to the effect of DOC, which decreases the availability of Hg_T^{2+} for methylation in the model. The user can assign the dissolved complexes that are available for methylation. Methylation can also be set as a function of sulfate concentration in the water column. If the user wants to eliminate the dependency of methylation on sulfate, K_4 may be given a value of zero in the menu.

Demethylation is assumed to occur in the water column and sediments. In the water column, demethylation is modeled as a light dependent abiotic process. It is modeled as being first order with respect to the concentration of dissolved CH_3Hg^+, and a function of the rate of light extinction in the lake. Thus demethylation in the water column primarily occur in the epilimnion. In sediments, demethylation is treated as a bacterial process, which operates on some or all of the dissolved CH_3Hg^+ in porewater. Sulfate and temperature are assumed to affect methylation, but not demethylation.

Diffusion is included in the model as a process occurring across the sediment/water interface and across the thermocline. Reduction of Hg_T to Hg^0 is included in the water column, but not the sediments. It is assumed that reduction is pH dependent, and that only a certain fraction of dissolved Hg_T^{2+} is available for reduction. This fraction is presently represented in the model by $Hg(OH)_2$. Therefore at higher pH values, rates of reduction of Hg_T^{2+} increase.

Volatilization of Hg^0 and CH_3Hg^+ are both included in the model. Volatilization of Hg_T is not included. Volatilization is calculated using two-phase film resistance

theory. The approach uses a piston velocity based on resistance in air and water, and the deviation of the air/water concentration ratio from equilibrium partitioning, to estimate the air/water flux.

The model can accommodate point source inputs of Hg_T^{2+} and CH_3Hg^+. Point source Hg loads are input to the epilimnion. Point source Hg loads are assumed to be Hg_T^{2+} and/or CH_3Hg^+. Local industrial sources of elemental mercury are not included in the model.

In the epilimnion, Hg_T^{2+} and CH_3Hg^+ are both partitioned between the dissolved phase and three particulate compartments: living phytoplankton, living zooplankton, and the remaining non-living suspended particles. In the hypolimnion, partitioning between dissolved and particulate phases also occurs, however in the model, all particles in the hypolimnion are assumed to be non-living. Elemental mercury is assumed to exist in dissolved phase only.

Concentrations of Hg_T^{2+} and CH_3Hg^+ in non-living suspended matter are estimated by assuming adsorption/desorption and using a partition coefficient. The user inputs a partition constant, which represents the ratio of the concentration of Hg on suspended non-living particles to all, or a fraction of, the dissolved Hg complexes. For all Hg_T^{2+}, this constant is based on the aquo Hg_T^{2+} ion. For CH_3Hg^+ it is based on inorganic (non-DOC-bound) complexes.

In the living phytoplankton, Hg_T^{2+} and CH_3Hg^+ concentrations are determined by the rates of uptake and losses. Uptake includes passive diffusion and possibly facilitated uptake. Losses are represented by cell growth/division and possibly depuration. Diffusion limited uptake may also occur. Since this is a steady-state model, conditions

are constant with time, single values emerge for the partitioning ratios for Hg_T^{2+} and CH_3Hg^+ in phytoplankton.

Passive diffusion involves the diffusion of various Hg complexes into a phytoplankton cell. Passive diffusion is combined with facilitated uptake and loss terms (growth, depuration) to arrive at a value for the partition constant between Hg in phytoplankton and dissolved Hg in water.

The option of facilitated uptake of Hg_T^{2+} and /or CH_3Hg^+ into phytoplankton cells is included in the model. This is used in combination with other processes affecting Hg uptake and losses in phytoplankton to estimate a partition ratio between phytoplankton and dissolved Hg_T^{2+} or CH_3Hg^+. The model is steady-state, and assumes constant values for parameters affecting uptake and losses of Hg in phytoplankton. This process is intended to represent the possibility that Hg_T^{2+} could be mistaken for other essential metals (e.g., iron, zinc) and enter the cell via transport pathways for these metals. The process may involve complexation of the metal at the cell surface and then transport into the cell. Depending on which complexes in solution exchange with the surface ligands, and the rate of exchange relative to the rate of incorporation into the cell, the transport rate could be a function of the concentration of the aquo ion (e.g., Hg^{2+}, CH_3Hg^+), or a function of the concentrations of several complexes (e.g., all inorganic complexes).

Methyl Hg and Hg_T^{2+} concentrations in zooplankton are calculated by multiplying the concentrations in phytoplankton times the factors, ratio of CH_3Hg^+ concentration in zooplankton/CH_3Hg^+ concentration in phytoplankton and ratio of Hg_T concentration in zooplankton/Hg_T concentration in phytoplankton, respectively. This approach is based

on the concept that zooplankton obtain the majority of their Hg in lakes from food, assumed to be phytoplankton.

Partitioning of Hg in the sediments (epilimnetic and hypolimnetic) is essentially treated in the same way as partitioning in the water column. Adsorption of Hg onto sediment solids is modeled identically to the partitioning of Hg onto non-living suspended particles in the water column. However, the values of the partition coefficients for sediments are different, thus reflecting the difference in adsorption characteristics between sediment solids and solids suspended in the water column.

The treatment of sulfides in the model is under development. There are several unresolved issues regarding the effects of sulfide on the aquatic Hg cycle. These include:

- Which sulfide/Hg_T^{2+} and sulfide/CH_3Hg^+ complexes form, and the appropriate complexation constants.

- Whether sulfide/Hg interactions are in fact reflected by thermodynamic equilibria

  Effects of iron and manganese on sulfide/Hg interactions (e.g., co-precipitation of Hg_T^{2+} with Fe

For these reasons, the model presently does not include sulfides in the simulations even if input data includes sulfides. The outputs for thermodynamic Hg speciation will always show zero concentrations for any sulfide/Hg complexes.

3.2 Data Sets Used

3.2.1 Water Column Hg, Sediment Deposition of Hg, Hg Concentrations in Surface Sediments and Hg in Aquatic Biota

Data from water column Hg, Hg settling from the water column, Hg in the sediment cores and Hg in aquatic biota were obtained by PTI Environmental Associates (Henry et al., 1995, Jacobs et al., 1995; Klein et al., 1995). Lake water samples were collected monthly from April and November 1992 at two stations located approximately in the centers of the north and south basins of Onondaga Lake. Unfiltered water samples were collected at each station from water depths of 0, 3, 6, 9, 12, 15, and 18 m during summer stratification (May – September) and from water depths of 3, 9, and 15 m during the remaining months (April, October – November) (Jacobs et al., 1995). Filtered water samples from the same depths were collected at one of the two station:

Lake water samples were collected from a fiberglass boat using a peristaltic pump (for analysis of total suspended solids (TSS), Fe, Mn and Hg species) or an acrylic Kemmerer sampler (for conventional analytes) Beginning with the 0-m depth, samples for analysis of TSS and metals were collected using Teflon bottles, packed on ice, and shipped overnight to the laboratory where they were filtered and preserved (Jacobs et al., 1995).

For dating purposes and estimation of net sedimentation, sediment cores were taken in the north and south basins to a depth of 2.5 m. Sediment traps approximately 20 cm in diameter were deployed from May through November of 1992, 2 m above the sediment in the north and south basins, to estimate gross sedimentation Traps were

sampled monthly for Hg_T concentration, CH_3Hg^+ concentration, and TSS. To avoid contamination, traps were made of acrylic plastic

Concentrations of Hg in phytoplankton, zooplankton, and benthic macroinvertebrates were determined using ultraclean sampling techniques and ultrasensitive analytical methods (Bloom, 1989; Watras and Bloom, 1992). Phytoplankton was sampled at two stations of the north and south basins of the lake. Samples were collected in Teflon® bottles from depths of 0, 3, and 6 m using a peristaltic-pumping system with Teflon® tubing. Three replicate samples were collected from each depth at each station. Samples were held at 4 °C and analyzed within 24 hours of collection. Phytoplankton were collected from samples of lake water using 0.8-µm quartz-fiber filters (Becker and Bigham, 1995)

Zooplankton were sampled at the same two stations as lake water and phytoplankton using a nonmetallic net (mesh size = 80 µm). Each sample was collected by a vertical net haul from a depth of 12 m and rinsed into Teflon® bottles. Within 8 hours of collection, cladocerans were transferred to Teflon® vials using glass pipets and frozen. Three replicate composite samples, each containing 20 cladocerans, were collected for each station (Becker and Bigham, 1995)

Fish were captured at various locations in the northern, western and southern parts of the lake. Captured individuals were either maintained whole or filleted immediately after collection using a stainless-steel knife. All whole bodies and fillets were frozen immediately after collection. Ten replicate whole bodies and 20 – 30 replicate fillets were collected for each target species (Becker and Bigham, 995). Mercury was

measured in fillets of seven fish species (gizzard shad, white perch, bluegill and smallmouth bass).

All Hg analyses were performed by Brooks Rand, Ltd., using cold vapor atomic fluorescence spectroscopy (Bloom and Fizgerald, 1988). Sediments were digested and analyzed for total Hg according to Bloom and Crecilius (1983, 1987). Total Hg in water samples was measured following bromium chloride oxidation (Bloom and Fizgerald, 1988). Analysis of total Hg samples followed the gold amalgamation technique (Gill and Fitzgerald, 1987). The CH_3Hg^+ concentration in sediments and water was measured by the ethylation technique following separation by ether extraction (Bloom, 1989) or distillation (Horvat et al., 1993a, b).

3.2.2 Dating of Sediment Deposition

For dating purposes a core was collected at the center of the lake and dated using ^{210}Pb by the Science Museum of Minnesota. Stratigraphic cores were sectioned at .0 cm intervals and analyzed for ^{210}Pb for dating purposes to determine rates of Hg deposition in sediments. ^{210}Pb activity was determined by measuring the activity of its grandaughter isotope, ^{210}Po, using alpha spectrometry (Bennet and Carpenter, 1979; Carpenter et al. 1981, 1982).

3.2.3 Mercury in Lake Inflows

Mass input data for Onondaga Lake were taken from Gbondo-Tugbawa (1997 This is considered to be most comprehensive investigation of the Hg influx to Onondaga Lake because sampling was conducted over a 12-month period. Clean sampling techniques (Fitzgerald and Watras, 1989; USEPA, 1995) were used to collect monthly water samples from October 1995 to September 1996 in selected tributaries including

Ninemile Creek, Onondaga Creek, Harbor Brook, Ley Creek, and the effluent discharged from METRO. Analytical protocols were used to analyze the tributary water samples for Hg_T (Gill and Fitzgerald, 1987). Methyl Hg analyses were done in accordance with Hovart et al. (1993) and Liang et al. (1994). Mean daily flow measurements for the major tributaries were obtained from the U.S. Geological Survey. However, the minor tributaries, lake water and sediments, and groundwater inputs to the lake were not sampled during this period.

3.2.4 Total Suspended Solids (TSS)

Suspended solid concentrations in the lake water columns (0, 4, 8, 12 and 16 m) were analyzed weekly from April 1995 to October 1995, while those in tributaries including Onondaga Creek, Ninemile Creek and the effluent discharged from METRO were biweekly analyzed from January 1995 to November 1995 by researchers at the Upstate Freshwater Institute (UFI) (Effler unpublished data). These data were used to conduct a TSS mass balance on the lake. Data of settling water column TSS were taken from Womble et al (1996).

3.2.5 Monitoring of Mercury in Fish

Fish collections from Onondaga Lake began in the fall of 1970 and have continued during summer for most years through the present. All collections were made by personnel of the Bureau of Fisheries, DEC. Fish were captured in gill nets and seines, measured, weighed, sometimes scales removed for aging, tagged with identifying numbers, and frozen in plastic bags at −20 °C prior to chemical analysis.

Preparation of the fish for analysis varied but generally the head and viscera were removed and the remainder ground in a food mill and homogenized by mixing in a

commercial food mixer. Current preparation methods (post – 1977) involve a standard filleting technique where one whole side of the fish, scales removed but with skin intact, is cut from behind the operculum to the tail. This fillet contains one pelvic fin and bones of half the rib cage. Excluded from the fillet are the vertebral column and the dorsal, pectoral, anal and caudal fins. Fish less than 150 mm in length are analyzed with just head and viscera removed (NYSDEC, 1985).

Chapter 4 - Results and Discussion

4.1 Synthesis of Mercury Data for Onondaga Lake

4.1.1 Mercury Chemistry in Onondaga Lake

The concentrations of Hg_T, CH_3Hg^+ and Hg_T^{2+} in Onondaga Lake in 1992 are summarized in Table 4. 1.A, 4. 1.B, 4.1.1.C and 4. 1.D. In this analysis inorganic Hg (Hg_T^{2+}) is defined as the difference between Hg_T and CH_3Hg^+. The mean concentrations ($\pm$ standard deviation) of Hg_T, CH_3Hg^+ and Hg_T^{2+} in the epilimnion were 5.70 ± 1.98 ng/L, 0.65 ± 0.42 ng/L and 5.05 ± 2.06 ng/L, respectively in 1992.

Table 4.1.1.A Monthly mean concentrations of Hg_T, CH_3Hg^+, Hg^{2+} and TSS, standard deviation and the mean fraction occurring in a particulate form in the epilimnion of Onondaga Lake, 1992

1992	Hg_T (ng/L) (% particulate Hg_T)	CH_3Hg^+ (ng/L) (% particulate CH_3Hg^+)	Hg_T^{2+} (ng/L) (% particulate Hg^{2+})	TSS (mg/L)
April	9.67±2.52 (64.9%)	0.33±0.09 (68.2%)	9.34±2.47 (64.7%)	9.16±1.93
May	3.75±0.89 (48.5%)	0.50±0.62 (77.7%)	3.25±0.77 (44.6%)	2.51±1.06
June	3.38±0.74 (47.8%)	0.54±0.30 (57.1%)	2.84±0.76 (46.0%)	1.49±0.27
July	4.86±1.10 (64.9%)	0.37±0.11 (68.0%)	4.50±1.12 (72.2%)	3.03±1.53
August	5.97±0.90 (64.9%)	0.37±0.17 (61.7%)	5.63±0.93 (33.3%)	4.96±1.96
September	6.59±1.16 (56.9%)	0.50±0.22 (63.0%)	6.08±1.27 (56.4%)	2.94±1.33
October	5.00±0.37 (56.0%)	1.19±0.43 (68.1%)	3.81±0.14 (52.2%)	4.71±0.67
November	6.38±1.13 (58.0%)	1.43±0.13 (45.4%)	4.95±1.10 (62.0%)	1.65±0.42
Year	5.70±1.98 (56.0%)	0.65±0.42 (60.5%)	5.05±2.06 (55.5%)	3.86±2.64

Table 4.1.1.B Monthly mean concentrations of Hg_T, CH_3Hg^+ and Hg^{2+} and standard deviation occurring in a dissolved and particulate form in the epilimnion of Onondaga Lake, 1992

1992	Hg_T Dissolved	Particulate	CH_3Hg^+ Dissolved	Particulate	Hg_T^{2+} Dissolved	Particulate
April			0.11±0.02	0.23±0.09		
May			0.11±0.05	0.39±0.57		
June			0.23±0.13	0.31±0.17		
July			0.12±0.07	0.25±0.06		
August			0.13±0.10	0.21±0.10		
September			0.19±0.10	0.32±0.15		
October			0.38±0.07	0.81±0.41		
November			0.79±0.09	0.63±0.09		

Concentrations of Hg_T and CH_3Hg^+ in the epilimnion were highly variable over the study period (1992). High concentrations of Hg_T were observed in April, August, September and November, with the highest value occurring in April (9.67 ± 2.52 ng/L) For CH_3Hg^+, the highest concentrations were observed in October and November coinciding with the turnover period. High concentrations of CH_3Hg^+ in the epilimnion during fall turnover are likely due to the mixing of the hypolimnetic waters with high concentrations of CH_3Hg^+. Concentrations of Hg_T, CH_3Hg^+ and Hg_T^{2+} were generally higher in the hypolimnion than the epilimnetic with mean values of 3.23 ± 6.97 ng/L, 4.97 ± 4.22 ng/L and 8.26 ± 4.91 ng/L, respectively in 1992.

Concentrations of TSS were generally below 4 mg/L throughout water column, with the exception of April and September/October. Elevated concentrations of TSS in April may be attributable to the high solids loads introduced to Onondaga Lake during the spring high flow period of 1992 (Jacobs et al. 1995). Elevated particle concentrations were also observed in the hypolimnion during September and October.

The elevated concentrations of Hg_T and Hg_T^{2+} in April are consistent with the elevated

TSS concentrations.

Table 4.1.1.C Monthly mean concentrations of Hg_T, CH_3Hg^+, Hg_T^{2+} and TSS, standard deviation and the mean fraction occurring in a particulate form in the hypolimnion of Onondaga Lake, 1992

1992	Hg_T (ng/L) (Particulate Hg_T)	CH_3Hg^+ (ng/L) (particulate CH_3Hg^+)	Hg^{2+} (particulate Hg^{2+})	TSS (mg/L)
April	17.50±16.26 (80.0%)	0.36±0.05 (63.4%)	17.15±16.21 (80.3%)	8.55±2.33
May	5.17±0.75 (59.0%)	0.90±0.51 (71.6%)	4.27±0.65 (56.4%)	3.48±0.85
June	6.47±2.05 (46.6%)	3.68±1.82 (35.3%)	2.78±1.60 (61.7%)	1.72±0.44
July	11.00±3.72 (76.3%)	5.40±2.32 (63.4%)	5.60±1.40 (80.3%)	2.90±2.97
August	17.35±1.40 (54.9%)	7.95±1.51 (55.8%)	17.15±16.21 (73.7%)	3.15±1.37
September	20.58±1.85 (62.8%)	7.72±2.68 (50.0%)	9.40±1.58 (54.3%)	6.53±5.31
October	17.70±N/A (41.0%)	N/A	10.10±N/A (85.1%)	7.60±0.42
November	5.75±0.49 (58.3%)	1.35±0.21 (61.9%)	4.40±0.28 (57.2%)	2.00±0.14
Year	13.23±6.97 (61.6%)	4.97±4.22 (45.1%)	8.26±4.91 (71.5%)	4.49±2.66

Table 4.1.1.D Monthly mean concentrations of Hg_T, CH_3Hg^+ and Hg^{2+} and standard deviation occurring in a dissolved and particulate form in the hypolimnion of Onondaga Lake, 1992

1992	Hg_T Dissolved	Hg_T Particulate	CH_3Hg^+ Dissolved	CH_3Hg^+ Particulate	Hg_T^{2+} Dissolved	Hg_T^{2+} Particulate
April	3.50±0.99	14.0±15.3	0.13±0.01	0.23±0.06	3.37±1.00	13.8±15.2
May	2.12±0.33	3.05±0.67	0.25±0.15	0.64±0.36	1.86±0.29	2.41±0.58
June	3.45±1.04	3.02±1.71	2.38±1.05	1.30±0.88	1.07±0.48	1.72±1.55
July	3.45±0.42	7.55±3.31	1.98±0.34	3.43±2.27	1.48±0.49	4.13±1.11
August	7.82±1.53	9.53±1.67	3.52±0.50	4.43±1.62	4.30±1.47	5.10±1.76
September	7.26±1.59	12.9±1.86	3.86±0.75	3.86±2.35	3.40±1.19	9.00±3.79
October	10.45±0.0	7.35±0.00	N/A	3.20±0.00	1.50±0.00	8.60±0.00
November	2.40±0.28	3.35±0.21	0.52±0.12	0.84±0.33	1.89±0.40	2.52±0.12
Year	5.09±3.1	8.15±4.59	2.93±2.98	2.24±1.66	2.36±1.17	5.91±4.21

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The highest values of Hg_T and CH_3Hg^+ in the hypolimnion were observed in September (20.58 ± 1.85 ng/L) and August (7.95 ± 1.51 ng/L), respectively. During the summer stratification, concentrations of Hg_T and CH_3Hg^+ increased in the hypolimnion. This pattern likely reflects the results of several processes including: 1) the mineralization/release of Hg associated with the recent deposition of particulate matter (Hurley et al., 1995), 2) the mobilization of Hg_T^{2+} and CH_3Hg^+ from recent sediments due to the formation of strong aqueous complexes of sulfide (Wang and Driscoll, 1995) and 3) for CH_3Hg^+, methylation that occurs under anaerobic conditions in the hypolimnion. Bloom and Effler (1990) reported a pattern of increasing concentrations of Hg with increasing depth in the lake.

Particulate matter plays an important role in the chemistry, partitioning and cycling of Hg in the water column of Onondaga Lake. The percent of Hg_T occurring in a particulate form ranged from 41.0 % to 80.0 %, while particulate CH_3Hg^+ ranged from 33.4 % to 77.7 % of total CH_3Hg^+ in the water column of Onondaga Lake. The empirical relationship between particulate Hg_T and TSS for the epilimnion was TSS (mg/L) = .44 x particulate Hg_T (ng/L) – 0.79; $r^2 = 0.48$ and for the hypolimnion was TSS (mg/L) = 0.46 x particulate Hg_T + 0.95; $r^2 = 0.48$. The relationship between particulate CH_3Hg^+ and TSS for the epilimnion was TSS (mg/L) = .4 x particulate CH_3Hg^+ (ng/L) – 4.27; $r^2 = 0.02$ and for the hypolimnion was TSS (mg/L) = -0.08 x particulate CH_3Hg^+ + 4.49; $r^2 = 0.002$. These calculations showed relatively strong positive correlation between particulate Hg_T and TSS in the epilimnion ($r^2 = 0.48$) and in the hypolimnion ($r^2 = 0.48$). Variations in CH_3Hg^+ were not correlated with TSS in the epilimnion ($r^2 = 0.02$) and

hypolimnion ($r^2 = 0.0002$) of Onondaga Lake. These values suggest that there is a stronger relationship between particulate Hg_T and TSS in Onondaga Lake than that between particulate CH_3Hg^+ and TSS.

Much of the particulate matter in the lake is of biological origin. Plankton could be an important determinant of patterns of Hg concentration (Hudson et al., 1994). Because of the high productivity of Onondaga Lake, factors affecting the biological activity, such as temperature, intensity of light, and input of nutrients, may influence the temporal and spatial variations in Hg concentrations (Wang and Driscoll, 1995).

4.1.2 Total Mercury (Hg_T) and Methyl Mercury (CH_3Hg^+) Mass Balance

Using data from previous studies (Chapter .4) on Hg_T, CH_3Hg^+ and TSS in inflowing streams and hydrologic data, water column Hg_T, CH_3Hg^+ and TSS data, sediment trap Hg_T, CH_3Hg^+ and TSS data, sediment Hg_T and CH_3Hg^+ and values of the sediment burial, Hg_T and CH_3Hg^+ mass balances were developed for Onondaga Lake. The description of the data set used in this complilation is given in Chapter 3

A. Total Mercury (Hg_T) Mass Balance

The mass balance of Hg_T in Onondaga Lake is shown in Figure 4. .2.A using a composite of the best available data. This analysis suggests that major tributaries including METRO and atmospheric deposition contributed 10.64 kg/year of Hg_T to the lake, while outflows and volatilization removed 4.67 kg/year of Hg_T from the lake. Of 10.64 kg/year external loads, tributaries including METRO contributed 10.5 kg/year of total Hg_T loading (98.7 %). Atmospheric deposition was assumed to be 0.14 kg/year, while the volatilization was assumed to be 0.15 kg/year. Both atmospheric deposition and volatilization were minor input and output in the Hg_T mass balance

Harbor Brook (0.07)
Ley Creek (0.28)
Onondaga Creek (1.41)
Ninemile Creek (4.41)
METRO (4.32)

Tributaries
(10.5)

Atmospheric deposition
(0.14)

Volatilization
(0.15)

Lake Outlet
(4.52)

Gross Sedimentation
(48.0)

Burial
(47.7)

Release from Hypolimnetic
Sediment
(1.97)
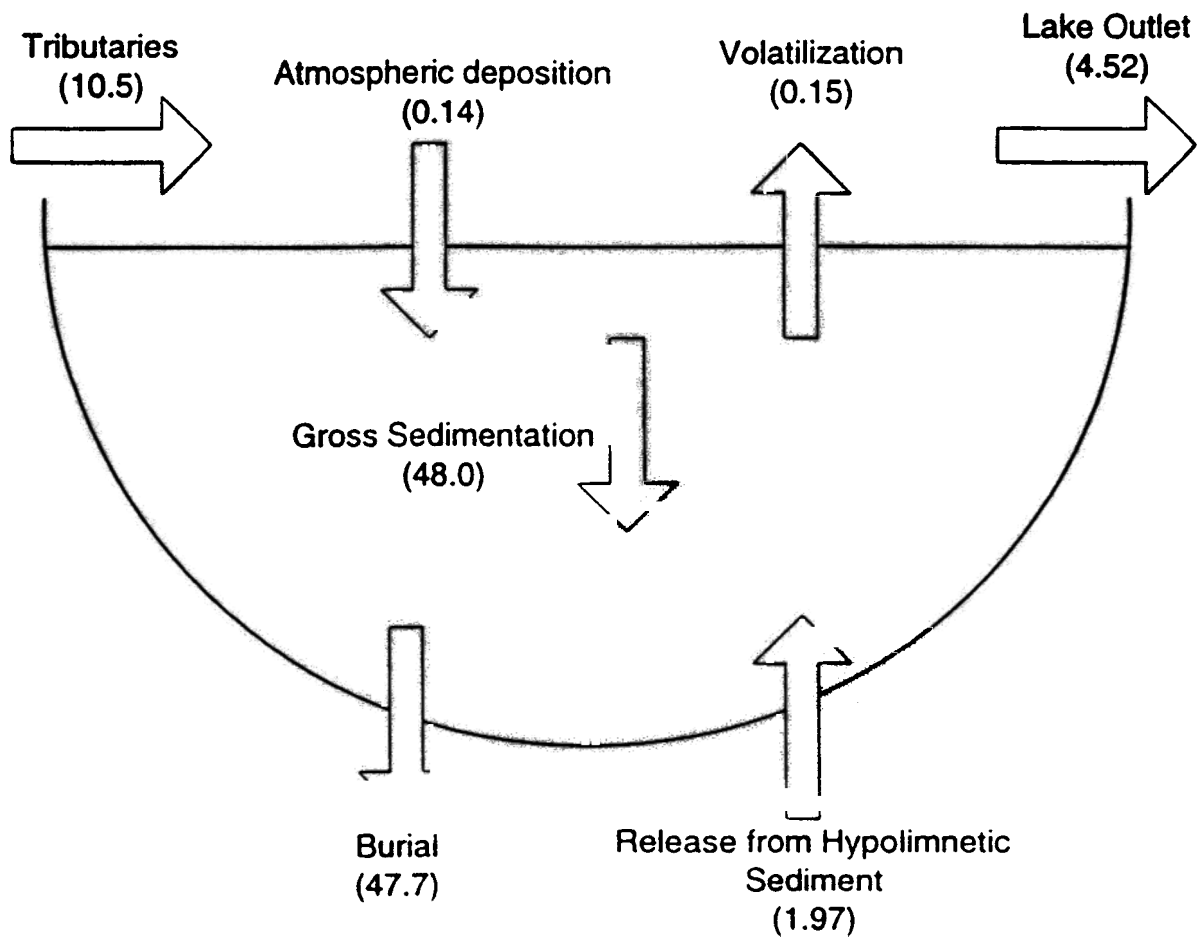
**Figure 4.1.2.A Total mercury (Hg$_T$) mass balance in Onondaga Lake
(in kg/year)**

The most distinguishing feature of the Hg_T budget for Onondaga Lake were the high values for gross sedimentation and sediment burial of 48 kg/year and 47.7 kg/year, respectively. These values were approximately five times greater than the amount of Hg_T that enters the lake (10.64 kg/year) from external inputs. These very large fluxes likely represent resuspension and redeposition of particulate materials, likely from the epilimnion. These large internal fluxes indicate that sediments are a major source of Hg_T contamination within the lake. Apparently resuspension of sediments supply large amounts of Hg_T into the water column and it is subsequently redeposited back to sediments. In addition, the internal rate of Hg_T release in the hypolimnion was .97 kg/year.

B. Methyl Mercury Mass Balance

The mass balance of CH_3Hg^+ in Onondaga Lake is shown in Figure 4. 2.B. Major tributaries including METRO contributed 0.45 kg/year. Internal production of CH_3Hg^+ from hypolimnetic sediments (methylation and release from sediment) was .01 kg/year. Outflows removed 0.30 kg/year of CH_3Hg^+ from the lake. The gross sedimentation .92 kg/year) was estimated from the sedimentation trap sampling. This value is about five times greater than the amount of CH_3Hg^+ that enters the lake from external sources (0.46 kg/year: 0.45 from tributaries and 0.006 from atmospheric deposition). Values of CH_3Hg^+ deposition in sediment traps and release of CH_3Hg^+ from hypolimnetic sediments suggest very high rates of CH_3Hg^+ production in the lake. In Rates of CH_3Hg^+ production are summarized for studies in the literature in Table 4. 2.B. The rates of CH_3Hg^+ production estimated for Onondaga Lake are much greater than other values reported in the literature for wetlands and other lake ecosystems. Rates of

Harbor Brook (0.008)
Ley Creek (0.02)
Onondaga Creek (0.09)
Ninemile Creek (0.15)
METRO (0.2)

Tributaries (0.45)   Atmospheric Deposition   Lake Outlet
                                   (0.006)   (0.3)

Gross Sedimentation
(1.92)

Burial   Release from Hypolimnetic
(0.2)   Sediments
                        (1.01)
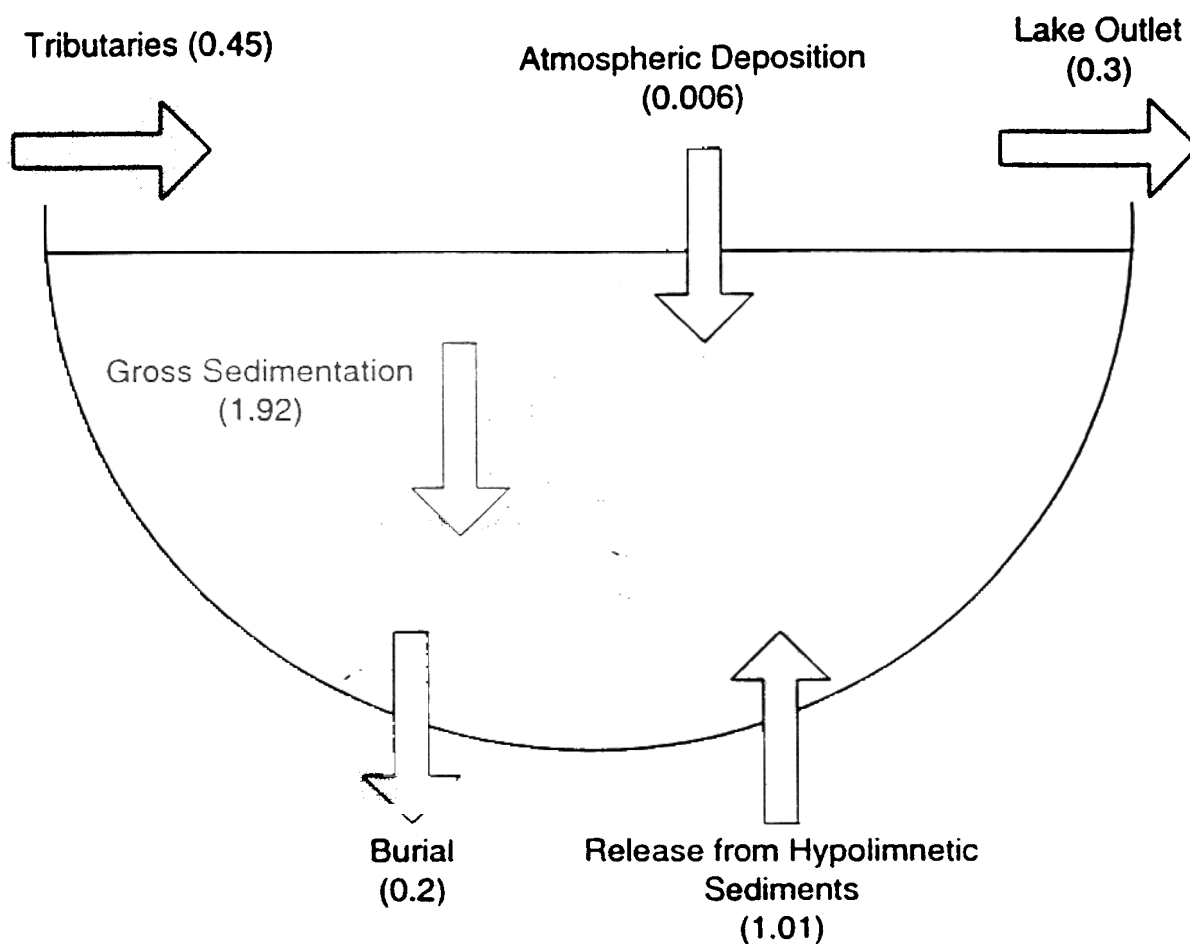
**Figure 4.1.2.B Methlmercury mass balance in Onondaga Lake
(in kg/year)**

burial of CH_3Hg^+ were relatively low which again is suggestive of elevated rates of internal production of CH_3Hg^+.

Table 4.1.2.B Comparison of CH_3Hg^+ production rates ($\mu g/m^2$-year).

Location	CH_3Hg^+ Flux	Reference
South Sweden	0.12	Lee and Hultberg (1990)
North Sweden	0.08 – 0.16	Lee et al. (1995)
Wisconsin	0.06 – 0.15	Krabbenhoft et al. (1995)
Ontario upland	0.007 – 0.098	St. Louis et al. (1994)
Ontario wetland	0.18 – 0.55	St. Louis et al. (1994)
Adirondack region, NY	0.17	Driscoll et al. (1998)
Onondaga Lake		Gbondo-Tugbawa and Driscoll (1998)
Watershed	0.1 – 0.24	
Lake	84	

4.1.3 Total Suspended Solids Mass Balance

From the above analysis, it is evident that the biogeochemistry of Hg in Onondaga Lake is closely coupled with particulate matter. As a result a preliminary TSS mass balance for the lake was developed for Onondaga Lake. An understanding of fluxes of TSS can provide insight on Hg transformations using empirical relationships with TSS. An additional Hg budget was developed based on TSS fluxes. The results of the TSS budget (Table 4. 3) showed that Ninemile Creek contributed the highest loading of TSS (4.05×10^6 kg/year; 44.13 %) to the lake. Onondaga Creek supplied the next highest TSS input (2.76×10^6 kg/year) contributing 29.09 % of TSS to the lake. These two tributaries accounted for about 75 % of the TSS loadings to Onondaga Lake. METRO effluent contributed 8.6×10^5 kg/year TSS load (9.40 %) to the lake. Harbor Brook and Ley Creek contributed 4.42×10^5 kg/year (4.62 %) and   7 kg/year (12.75 %) TSS to the

lake, respectively. The total TSS load from tributaries including METRO was 9.17×10^6 kg/year.

Table 4.1.3 Loads of total suspended solids (TSS) and % contribution to the total load of Onondaga Lake.

Tributaries	TSS loading (kg/year)	Mean % Contribution to Lake
	4.24×10^5	4.62
	1.17×10^6	12.75
	2.67×10^6	29.09
	4.05×10^6	44.13
	8.63×10^5	9.40
Total Inputs	9.17×10^6	N/A
Outflow	1.35×10^6	N/A

The two sinks for TSS in Onondaga Lake were gross sedimentation (5.56×10^7 kg/year) and lake outflow .35 $\times 10^6$ kg/year). Of these losses, gross deposition represents 98 % of the total sinks. The flux of TSS in sediment traps was much greater than loads from tributaries (9.17×10^6 kg). Therefore, it was assumed that the difference between input loads and output loads was due to the internal production of TSS (4.63×10^7 kg/year) in Onondaga Lake. Internally produced particles include phytoplankton and inorganic precipitates (e.g., $CaCO_3$ particles) (Driscoll et al., 1993; Effler and Johnson, 1987). The sediment burial and mineralization were 3.99×10^7 kg/year and .32 $\times 10^6$ kg/year, respectively. The mass balance of TSS in Onondaga Lake is shown in Figure 4.1.3

The dynamics of the phytoplankton are an important regulator of the particle concentrations of the upper waters of the lake (Effler et al., 1996). According to Effler 1996), approximately 85% of the total particle cross sectional area per unit volume

Harbor Brook (4.42×10^5)
Ley Creek (1.17×10^6)
Onondaga Creek
(2.67×10^6)
Ninemile Creek
(4.05×10^6)
METRO (8.63×10^5)

Lake Outlet
(1.35×10^6)

Tributaries
(9.17×10^6)

Sedimentation
(5.56×10^7)

Internal Production
(4.63×10^7)

Burial
(3.99×10^7)

Mineralization
(1.32×10^6)
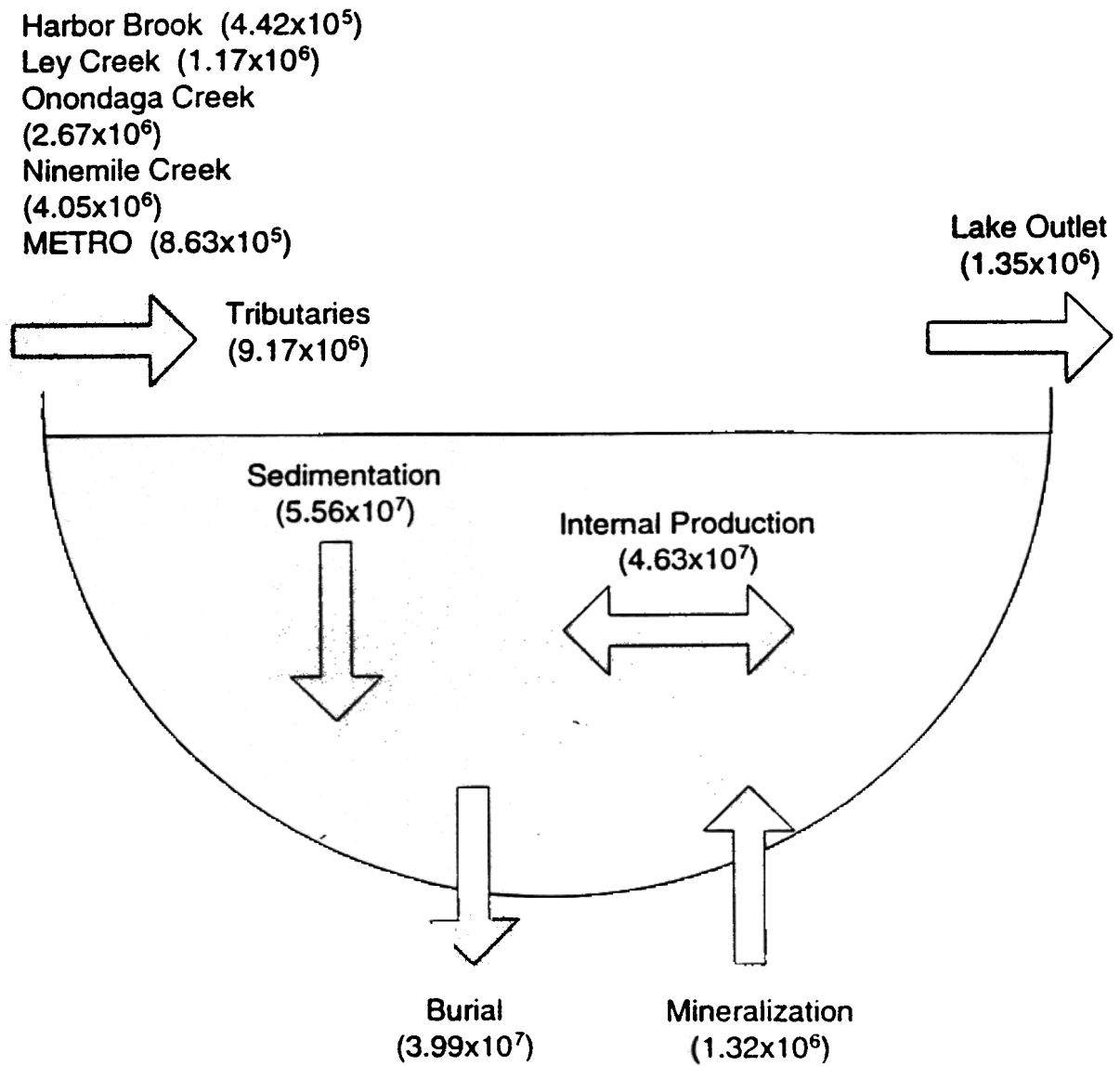
Figure 4.1.3 Total suspended solids (TSS) mass balance for Onondaga Lake (in kg/year)

(PAV) of the upper waters of Onondaga Lake in 1987 was associated with in-lake processes (Effler, 1996). About 60% was associated with biological (e.g., phytoplankton) production, 25% was attributed to inorganic particle (e.g., $CaCO_3$) formation. The remaining 15% was received from tributary inputs. These estimations are very similar to the TSS budget for this study. 83 % of total TSS was derived from internal production of particles, while 17 % was obtained from external source.

4.1.4 Partition Coefficients

The partition coefficient (K_d) quantifies the tendency of the contaminant (Hg species for this study) to associate with solid matter. The partition coefficient is calculated as following.

$$Partition\ coefficient = \frac{particulateHg\ /\ TSS}{dissolvedHg}$$

Thus, for weakly sorbing contaminants (low K_d) in systems with low suspended solids, the contaminant will be predominantly in dissolved form. For strong sorbers in turbid systems, the contaminant will be strongly associated with suspended solids.

The partition coefficients of Hg_T, CH_3Hg^+ and Hg_T^{2+} in the water column (epilimnion and hypolimnion) of Onondaga Lake were calculated in this study. The logarithm values of Hg species/TSS partition coefficients in the lake were very high. Partition coefficients showed no strong patterns with depth or season (Table 4.1.4.A and Table 4 4.B). There were also few differences in the partition coefficients for Hg_T^{2+} and CH_3Hg^+. The only noticeable pattern was a maximum in the partition coefficients for both CH_3Hg^+ and Hg_T in the hypolimnion in early summer (May-July) followed by a decrease until October and September, respectively. This subtle shift in the partitioning

of Hg may be due to the accumulation of sulfide in the lower waters and the formation of strong aqueous complexes of Hg^{2+} and CH_3Hg^+ (Wang and Driscoll, 1995).

Table 4.1.4.A Logarithm partition coefficients (L/kg) in the epilimnion of Onondaga Lake.

Date	Hg_T	CH_3Hg^+	Hg_T^{2+}
April, 1992	5.22±0.24		5.22±0.25
May, 1992	5.62±0.28		5.59±0.33
June, 1992	5.82±0.16		5.80±0.18
July, 1992	5.93±0.28		5.93±0.30
August, 1992	5.15±0.20		5.13±0.21
September, 1992	5.65±0.27		5.64±0.29
October, 1992	5.43±0.12		5.37±0.15
November, 1992	5.92±0.24		5.99±0.27
Average, 1992	5.59±0.22	5.71±0.21	5.58±0.25

Table 4.1.4.B Logarithm partition coefficients (L/kg) in the hypolimnion of Onondaga Lake.

Date	Hg_T	CH_3Hg^+	Hg_T^{2+}
April, 1992	5.67±0.38	5.31±0.05	5.68±0.39
May, 1992	5.62±0.16	5.86±0.27	5.57±0.18
June, 1992	5.70±0.34	5.51±0.30	5.93±0.63
July, 1992	6.06±0.19	5.80±0.37	6.41±0.05
August, 1992	5.59±0.28	5.60±0.32	5.58±0.33
September, 1992	5.47±0.45	5.22±0.31	5.64±0.57
October, 1992	4.96±N/A	4.68±N/A	5.86±N/A
November, 1992	5.84±0.05	5.91±0.25	5.82±0.15
Average, 1992	5.61±0.26	5.49±0.27	5.81±0.33

The K_d values of Hg_T and CH_3Hg^+ were generally greater in the epilimnion than those in the hypolimnion. However, the K_d values for Hg^{2+} were generally greater in the hypolimnion than those in the epilimnion. For Hg_T, the average of log K_d was 5.59 L/kg and 5.61 L/kg for the epilimnion and the hypolimnion, respectively. These results are in good agreement with that observed by Hurley et al. 1994) for Little Rock Lake (4.5

5.7) and by Stordal et al. (1996) in laboratory experiments (5.4 – 5.7). However, these values are slightly higher than the results obtained by Stordal et al. (1996) in Texas estuaries (4.6 – 5.2).

4.1.5   Estimates of Hg_T and CH_3Hg^+ Fluxes from TSS

Concentrations of Hg_T and CH_3Hg^+ in particulate matter in tributaries, the water column (epilimnion and hypolimnion), sedimenting material and surface sediments are shown in Table 4.1.5.A.

Table 4.1.5.A Mean concentrations of particulate Hg_T and CH_3Hg^+ ($\mu g\ Hg/g$ TSS) and standard deviation (std) in different systems of Onondaga Lake.

		Hg_T	CH_3Hg^+
Tributaries	Ninemile Creek	0.4	0.010
	Onondaga Creek	0.1	0.006
	METRO	1.8	0.021
	Other tributaries	0.2	0.004
Water Column	Mean ± std	2.8 ± 2.1	0.800 ± 1.200
Sediment Trap	Mean ± std	1.3 ± 0.01	0.070 ± 0.005
Surface Sediment	Mean ± std	1.8 ± 1.1	0.006 ± 0.007

The concentration of Hg_T in particulate matter was relatively low in tributaries, ranging from 0.1 $\mu g/g$ for Onondaga Creek to 0.4 $\mu g/g$ for Ninemile Creek and 8 for METRO. There was a marked enrichment in the Hg content of particulate matter from the tributaries to the lake, as evident by high Hg content in the water column particles (2.8 $\mu g/g$), sedimenting particles 3 $\mu g/g$) and surface sediments .75 $\mu g/g$). This pattern of enrichment of Hg content of particulate matter seems in conflict with large internal rates of particle production for the lake. Indeed, if external inputs of Hg are assumed to completely partition to the solids supplied to Onondaga Lake (internal and external), the Hg content of particulate matter in the lake would be 0.23 $\mu g/g$ This value is

approximately an order of magnitude than the measured in-lake values. Again this

discrepancy is suggestive of an internal sediment source of Hg to the water column of the

lake. From the TSS mass balance and concentrations of Hg_T and CH_3Hg^+ associated with

particulate matter, it is possible to estimate Hg_T and CH_3Hg^+ mass fluxes associated with

particulate matter. Loadings of TSS multiplied times concentrations of Hg_T and CH_3Hg^+

associated with particulate matter in particulate matter yield fluxes of Hg associated with

particulate matter. These fluxes are compared with the mass balances of Hg_T and

CH_3Hg^+ presented above in Table 4.1.5.B

Table 4.1.5.B Comparison of fluxes of Hg_T and CH_3Hg^+ (in kg/year) derived from TSS fluxes with mass balances of Hg_T and CH_3Hg^+.

	Fluxes from TSS		Mass Balance (4.1.2)	
	Hg_T	CH_3Hg^+	Hg_T	CH_3Hg^+
Tributaries	2.38	0.07	10.5	0.36
Gross Sedimentation	74.60	3.89	48.0	1.92
Burial	69.72	0.25	47.7	0.20
Outlet	3.83	1.11	4.52	0.30

The tributary fluxes from TSS (2.38 kg/year and 0.07 kg/year for Hg_T and CH_3Hg^+,

respectively) were much less than observed fluxes (10.5 kg/year for Hg_T and 0.36 kg/year

for CH_3Hg^+). This discrepancy suggests that much of the input of Hg to Onondaga Lake

occurs in a dissolved form. Fluxes of sedimentation (74.60 kg/year and 3.89 kg/year for

Hg_T and CH_3Hg^+, respectively) and burial (69.72 kg/year and 0.25 kg/year year for Hg_T

and CH_3Hg^+, respectively) from TSS were somewhat greater than the observed sediment

flux (48 kg/year for Hg_T and .92 kg/year for CH_3Hg^+) and burial flux (47.7 kg/year for

Hg_T and 0.199 kg/year for CH_3Hg^+). The discrepancy between measured and calculated

values based on the TSS might be indicative of errors or uncertainty in either or both budgets. Again these high values might indicate that there is recycling of particulate Hg prior to incorporation in the sediments.

4.1.6 Mercury Concentration and Bioconcentration in Aquatic Species

Historical and current discharges of Hg to Onondaga Lake, New York, have resulted in elevated Hg concentrations in lake fishes. At the same time, the distribution of Hg in aquatic food webs has received considerable attention because of the tendency for CH_3Hg^+ to bioaccumulate in organisms.

A. Bioaccumulation of Mercury in the Aquatic Food Chain of Onondaga Lake.

Bioaccumulation is the process by which organisms (including humans) can take materials more rapidly than their bodies can eliminate. The values of Hg_T, CH_3Hg^+, Hg_T^{2+} and the % of Hg_T occurring as CH_3Hg^+ were calculated at each level of a food chain (Table 4 .6.A).

Concentrations of Hg in aquatic biota and the fraction of Hg occurring as CH_3Hg^+ increase with increasing trophic level. This pattern can be explained by biomagnification, which is the incremental increase in concentration of a contaminant at each level of a food chain. This phenomenon occurs because the food source for organisms higher on the food chain is progressively more concentrated in Hg, thus magnifying bioaccumulation rates at the top of the food chain. The bioaccumulation generally increases the longer an organism lives, so that larger, long-lived predatory game fish will likely have the highest Hg concentrations and much of this Hg occurs in the highly toxic CH_3Hg^+ form. Adding to this problem is the fact that Hg concentrates in the muscle tissue of fish (Grieb et al., 1990). So, unlike organic contaminants (e.g. PCBs.

dioxins) which concentrate in the skin and fat, Hg cannot be filleted or cooked out of consumable game fish.

With increases in bioaccumulation of Hg with each level of a food chain, the percent of CH_3Hg^+ also increased, from phytoplankton (5.3×10^{-6} µg/g, 20 % of CH_3Hg^+) to omnivore (0.78 µg /g, 97 % of CH_3Hg^+).

Table 4.1.6.A Bioaccumulation of mercury in the aquatic food chain of Onondaga Lake.

	Hg_T (µg/g)	CH_3Hg^+ (µg/g)	Hg_T^{2+} (µg/g)	% of methyl mercury
Water	2.5×10^{-6}	3.0×10^{-7}	2.0×10^{-6}	10
Phytoplankton	5.3×10^{-6}	1.0×10^{-6}	4.0×10^{-6}	20
Zooplankton	1.5×10^{-3}	4.4×10^{-5}	1.1×10^{-3}	29
Planktivore (gizzaed shad)	0.23	0.20	0.03	87
Omnivore (carp, cat fish and white perch)	0.78	0.75	0.03	97
Piscivore (walleye)	N/A	2.27	N/A	N/A

The percentage of Hg_T occurring as CH_3Hg^+ varied throughout the lake food web and increased in higher trophic levels. The results of this study conform the conclusions of previous studies that CH_3Hg^+ is more efficiently transferred to higher trophic levels of aquatic food chains than is Hg_T^{2+} (Boudou and Ribeyre, 1981, 1985; Watras and Bloom, 1992).

B. Bioconcentration Factors

The bioconcentration factor (BCF) quantifies the tendency of the contaminant (Hg species for this study) to associate with living organisms. The bioconcentration factor is calculated as following:

$$BioconcentrationFactor(BCF) = \log\left(\frac{Hg\ Species - fish}{Hg\ Species - water}\right)$$

The BCF for phytoplankton, zooplankton, gizzard shad (planktivore), blue gill (benthivore), white perch (omnivore) and walleye (piscivore) in Onondaga Lake were calculated in this study (Table 4.1.6.B).

Table 4.1.6.B Bioconcentration factors (L/kg) for CH_3Hg^+ and Hg_T^{2+} in aquatic organisms of Onondaga Lake

Species	Log BCF (CH_3Hg^+)	Log BCF (Hg_T^{2+})
Phytoplankton	-0.33	0.007
Zooplankton	2.30	0.270
Gizzard Shad (planktivore)	4.96	4.130
Blue Gill (benthivore)	5.15	4.130
White Perch (omnivore)	5.66	3.980
Walleye (piscivore)	6.01	N/A

The log BCF values for CH_3Hg^+ increased markedly from phytoplankton (-0.33 L/kg) to zooplankton (2.30 L/kg) to fish (4.91 to 6.01 L/kg). These data reveal patterns of CH_3Hg^+ bioaccumulation depending on fish food sources. The planktivore, gizzard shad, exhibited the lowest BCF of the fish studied. The benthivore, blue gill, and the omnivore, white perch, showed intermediate values of log BCF's (5.15 and 5.66 L/kg, respectively). Finally, the piscivore, walleye, exhibited the largest BCF of the fish species in Onondaga Lake.

The log BCF values for Hg_T^{2+} were smaller than those for CH_3Hg^+. Furthermore, the log BCF values for Hg_T^{2+} decreased from benthivore blue gill (4 3 L/kg) to omnivore white perch (3.98 L/kg). This results suggests that CH_3Hg^+ is much more easily

bioaccumulated than Hg_T^{2+} in the aquatic organisms and the percentage of Hg_T occurring as CH_3Hg^+ increases in higher trophic levels (omnivore and piscivore).

C. Fish Hg Concentrations with Fish Age

Mercury concentrations in fish (smallmouth bass and white perch in Onondaga Lake) were calculated of different age classes (Table 4.1.6.C, Figure 4.1.6.C.A, and Figure 4.1.6.C.B).

Table 4.1.6.C Mean Hg concentrations and standard deviation in smallmouth bass and white perch of different age classes.

Age of fish	(1974-1994) Smallmouth bass Hg ($\mu g/g$)	(1973-1992) White perch Hg ($\mu g/g$)
2	0.54 ± 0.31	0.66 ± 0.31
3	0.85 ± 0.29	0.91 ± 0.28
4	0.96 ± 0.32	0.80 ± 0.33
5	1.15 ± 0.42	0.91 ± 0.33
6	1.27 ± 0.52	0.95 ± 0.38
7	1.32 ± 0.48	1.20 ± 0.44
8	1.62 ± 0.44	1.12 ± 0.49
9	1.55 ± 0.54	1.55 ± 0.72
10	1.82 ± 0.77	1.69 ± 0.64
11	1.70 ± 0.45	N/A

As observed in other studies, concentrations of Hg in fish tissue increased with increasing fish age class in Onondaga Lake (Driscoll et al. 1994). The 10 year age class for smallmouth bass (82 $\mu g/g$) had almost two times higher Hg concentration than 3 year age class (0.85 $\mu g/g$), and the 10 year age class white perch (1.69 $\mu g/g$) had about twice higher Hg concentration than the 3 year age class (0.91 $\mu g/g$).
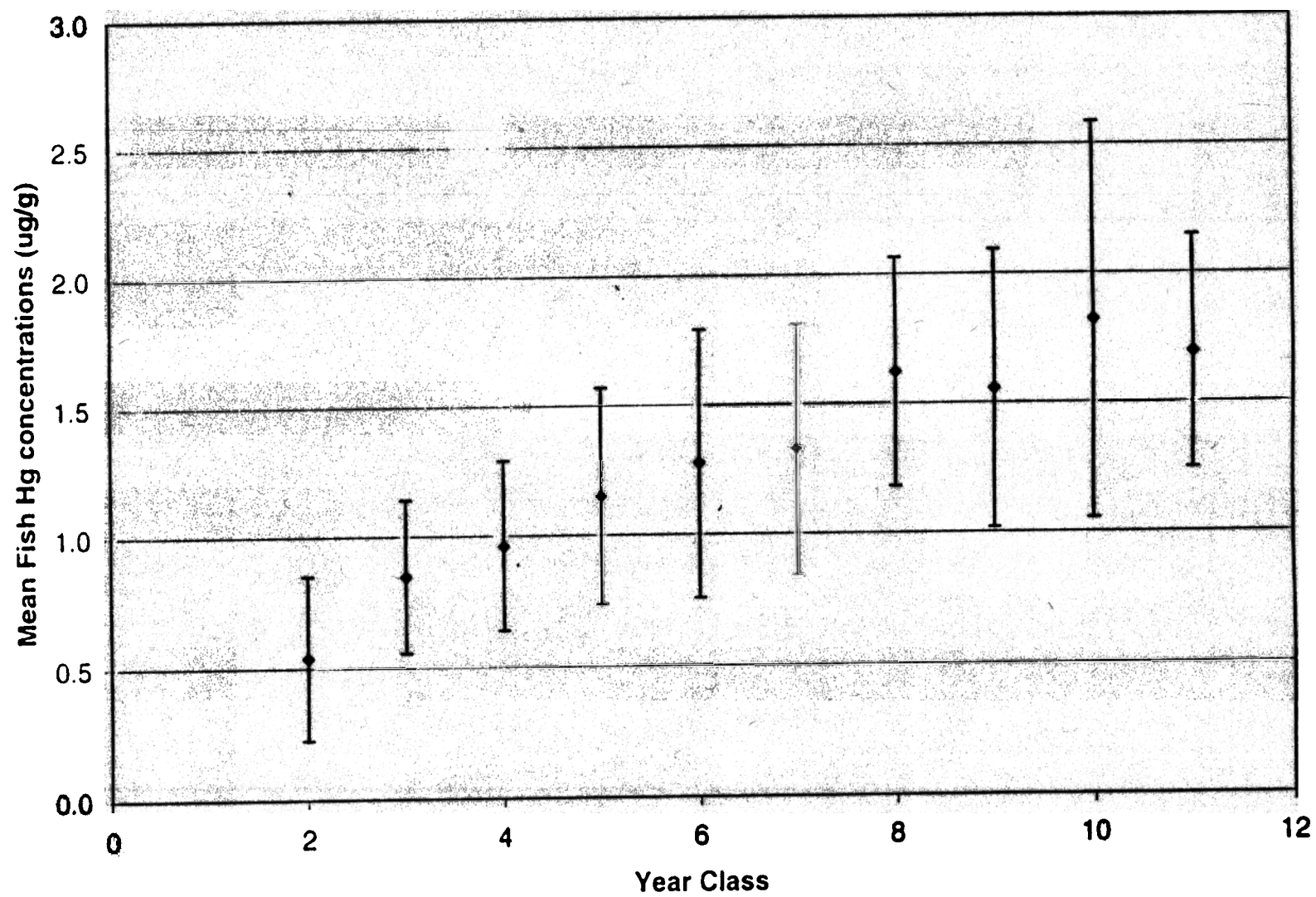
Figure 4.1.6.C.A Concentrations and standard deviations of Hg in smallmouth bass in different age classes
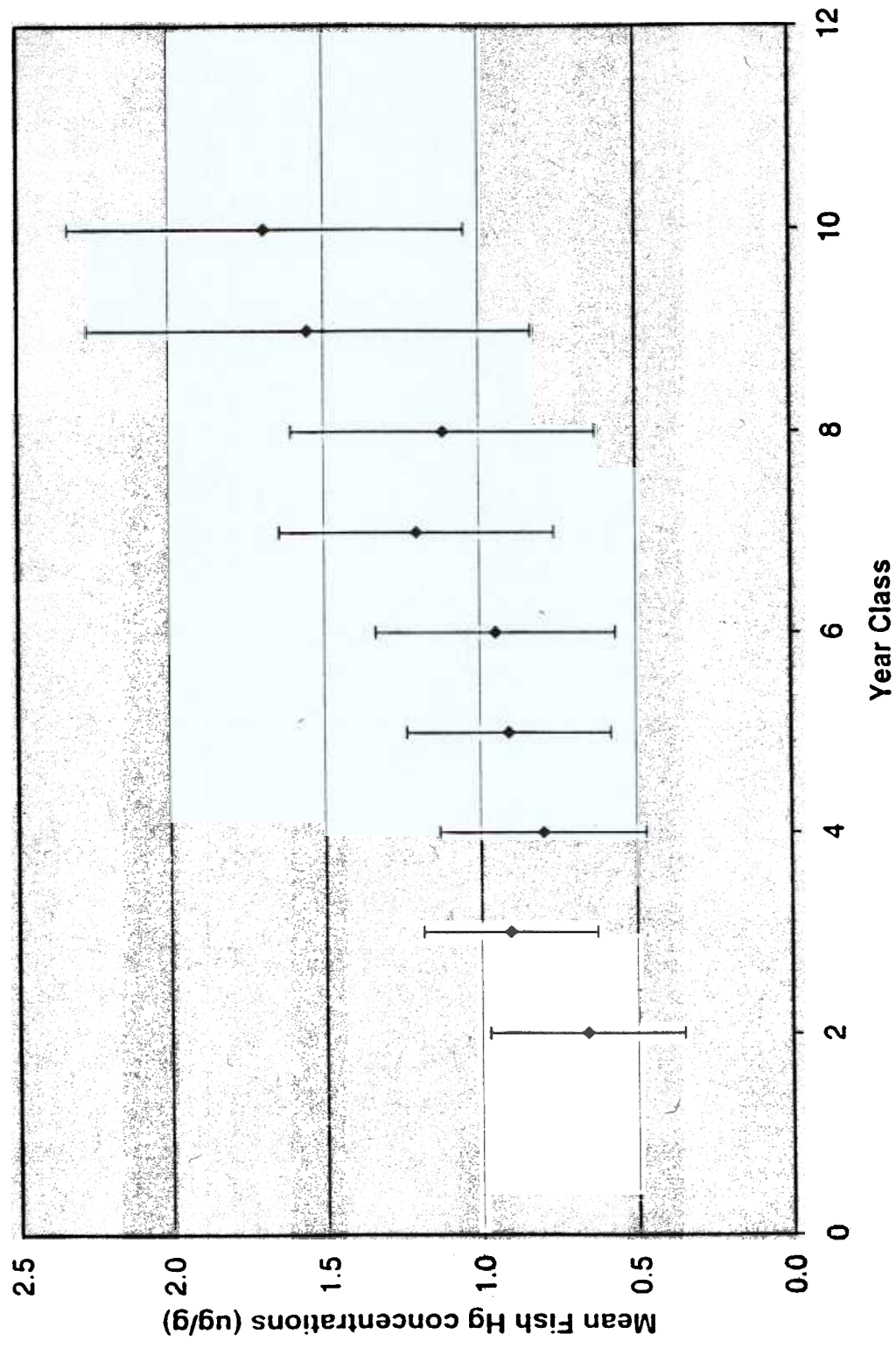
Figure 4.1.6.C.B Concentrations and standard deviations of Hg in white perch in different age classes

Understanding food sources for smallmouth bass and white perch help provide insight on the patterns of Hg concentrations in different age classes. Smallmouth bass juveniles initially feed on crustaceans and aquatic insects, which older age-classes prey on small fish as they grow larger (http://www.pvisuals.com). Crayfish are the favored food, but smallmouth bass also eat larval and adult insects, frogs, and tadpoles, and a variety of small fish (http://www.pvisuals.com). This pattern of changing food source with age help explains the increases in Hg concentration in the fish tissue of older age classes.

White perch have been found to eat the eggs of walleye, other white perch and possibly other species as well. Fish eggs are an important component of the diet of white perch in the spring months. This diet is unique in that eggs are eaten for a comparatively long time. They also feed heavily on minnows (http://www.seagrant.wisc.edu).

D. Smallmouth Bass Hg Concentrations between 1975 and 1996.

The Hg concentrations of smallmouth bass (4-6 age class) for approximately last 20 years were calculated using data from NYSDEC (Table 4 .6.D and Figure 4 .6.D).

Table 4.1.6.D The Hg concentrations of smallmouth bass (4-6 age class) over time.

Year	Hg concentration (μg/g)	Year	Hg concentration (μg/g)
	1.20 ± 0.27	1988	1.45 ± 0.35
	0.65 ± 0.05	1989	2.13 ± 0.57
	1.31 ± 0.01	1991	0.77 ± 0.11
	0.94 ± N/A	1992	0.72 ± 0.07
	1.25 ± 0.17	1995	1.36 ± 0.29
	1.05 ± 0.17	1996	0.96 ± 0.11
	1.71 ± 0.09		
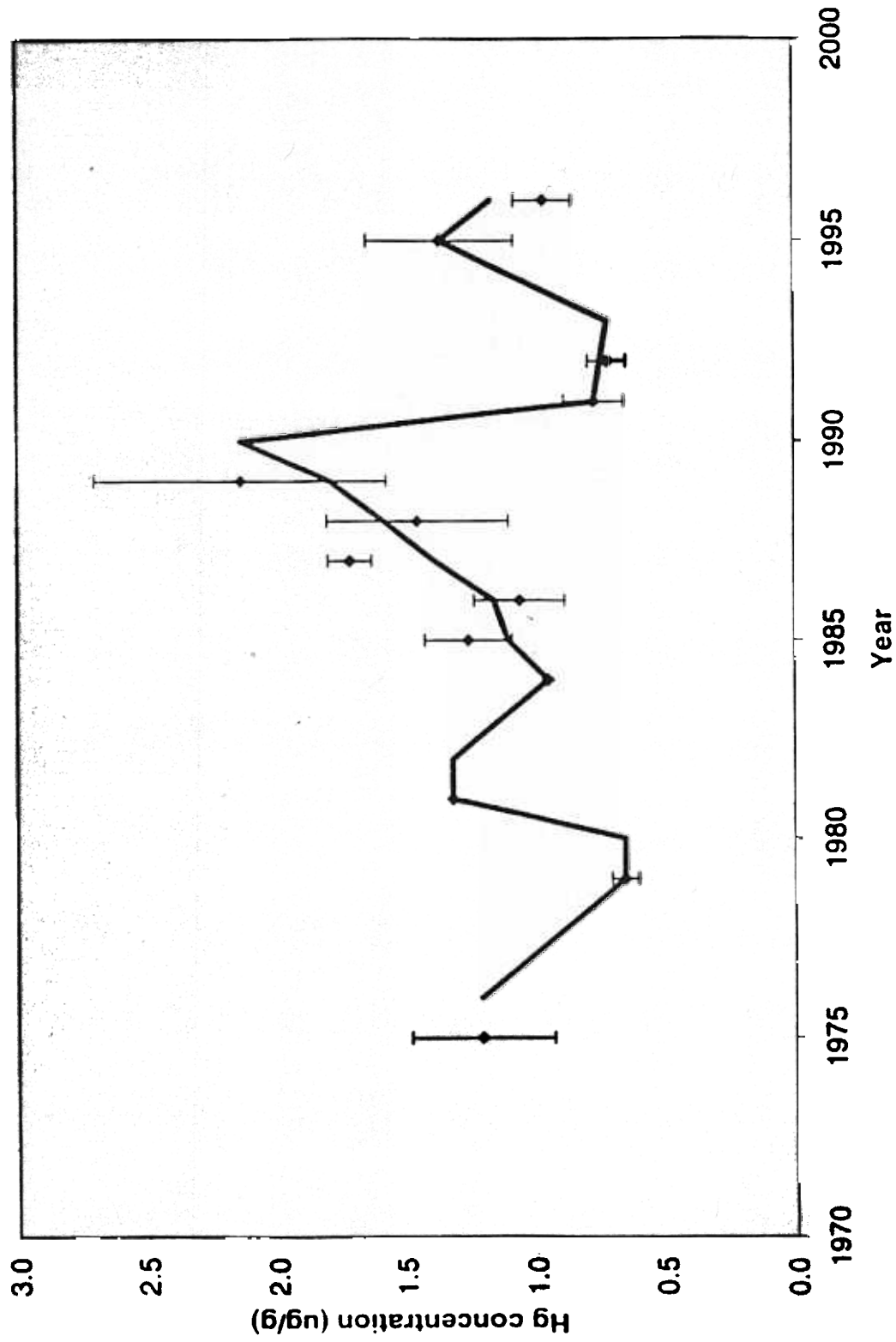
Figure 4.1.6.D Concentrations of Hg in smallmouth bass (4 – 6 age class) between 1975 and 1996

As mentioned in Chapter 1.4, after the closure of the soda ash manufacturing, a marked increase in Hg concentrations in smallmouth bass (up to 2.13 ppm in 1989) was observed.

There are several factors that may contribute to the step increase in fish Hg concentrations that followed closure of the chemical facility. After the closure there were marked reductions in inputs of Ca^{2+}, Na^+ and Cl^- to the lake. This resulted; 1) decreases in the precipitation of $CaCO_3$ and therefore a decrease in the settling velocity of particles and a decrease in particle deposition from the water column (Womble et al., 1996), 2) decreases in the precipitation of $CaCO_3$ resulted in increases in lake pH from 7.82 to 8.22 and 3) decreases in inputs of salt resulted in a increase in zooplankton populations and therefore a decrease in the deposition of organic paricles. The Cl^- concentrations in Onondaga Lake decreased approximately 70%. According to Ponce and Bloom (1990), fish bioaccumulate CH_3Hg^+ in inverse proportion to the water pH. This effect may be magnified further up the food chain. The marked decrease in Cl^- concentrations in the lake could have a similar effect as decreased pH, in that less of the CH_3Hg^+ becomes complexed into negatively charged ligands, which might be more bioavailable. Decrease in the settling velocity of particles may diminish the transport of Hg to the hypolimnion. A decrease in particle concentrations due to increased zooplankton grazing may reduce particle binding of Hg and enhance the bioavailabilty of Hg. Either of these mechanisms could explain the marked increase of Hg concentrations in smallmouth bass after 1986.

According to Becker and Bigham (1995), Hg concentrations in fillets of Onondaga Lake fishes have declined substantially from the values found in the early 1970s. Concentrations of Hg in white perch and smallmouth bass were about 5 µg/g and 2 µg/g in the early 1970s, respectively In 1992, concentrations of Hg in white perch and

smallmouth bass were > 1 μg/g and < 1 μg/g, respectively. They indicated that the general decline of Hg concentrations in fish tissue since the early 1970s parallels the substantial reductions in Hg discharges to Onondaga Lake that have resulted from various regulatory actions initiated in 1970.

4.2 Applications of Regional Mercury Cycling Model (R-MCM)

A. Model Calibration

The Regional Mercury Cycling Model (R-MCM) was used to simulate the mass balance of Hg_T and CH_3Hg^+ in the lake. This is a steady-state mechanistic model. designed to simulate the biogeochemical cycling of Hg in lakes. Input parameters include lake/watershed physical characteristics. water chemistry, atmospheric deposition and aquatic biomass. Most of these parameters were obtained from Effler (1996). Atmospheric deposition was estimated based on values of 10 μg Hg_T/m^2-year (Fitzgerald et al., 1991) and 0.016 μg CH_3Hg^+/m^2-year (Fitzgerald et al., 1991) in wet deposition. applied to the lake surface area. A dry deposition flux of Hg_T of 3.5 μg/m^2-year (Fitzgerald et al 1991) was assumed in the model. Groundwater flux was estimated from concentrations of Hg in groundwater (Jacobs et al., 1995) applied to the expected groundwater flow into the lake (Effler, 1996).

The major input parameters used in this study are summarized in Table 4.2.A. Particle settling velocity in epilimnion and hypolimnion were increased (2 m/day to 3 m/day) to match measured values reported Onondaga Lake based on TSS values in the epilimnion (Effler and Whitehead, 1995) and TSS deposition in sediments traps (Womble et al. 1996). The partition coefficient of Hg^{2+} in the hypolimnion (5 x 10^{10} m^3/g to 5

$x10^{11}$ m³/g) was adjusted from default the value to account for the strong binding of Hg_T^{2+} with sulfide (Wang and Driscoll, 1995). The model was also calibrated using Hg^0 concentrations in the water column observed by Bloom and Effler (1990). Because the model tended to predict high Hg^0 concentrations, rates of demethylation in hypolimnetic sediments (0.0001 to 0.000001 m²/g TOC-day) and rates of Hg^{2+} methylation in epilimnetic and hypolimnetic sediment (0.0003 to 0.00003 m²/g TOC-day) were adjusted from default values so that model simulated values matched measured water column Hg^0 concentrations. Default values for the model were used for all other parameters (Tetra Tech, 1996).

With the epilimnetic seston concentrations (TSS), it was assumed that about 70 % of epilimnetic seston settle (input called EpiDeadPart), while 20 % was living phytoplankton and 10 % was living zooplankton. The following proportions were maintained in the inputs to epilimnetic sediments: epilimnetic seston : burial velocity mineralization were equal to 1: 0.28 : 0.014. Similarly, for hypolimnetic sediments, the following proportions were maintained: hypolimnetic seston : burial velocity mineralization rate were equal to 0.003 (Harris, Tetra Tech Inc. unpublished).

Table 4.2.A Modified input parameters for this study.

Input parameters	Default values	Modified values for this study
Particle settling velocity in epilimnion and hypolimnion	2 m/day	3 m/day
Partition coefficient of Hg_T^{2+} (hypolimnion)	5×10^{10} m³/g	5×10^{11} m³/g
Demethylation rates in hypolimnetic sediments	0.0001 m²/g TOC – day	0.000001 m²/g TOC - day
Hg^{2+} methylation in Epilimnetic and hypolimnetic sediments	0.0003 m²/g TOC – day	0.00003 m²/g TOC - day

The model was used to predict Hg concentrations in the water column, sediments and smallmouth bass in the lake. These values were compared to measured values observed in recent studies. To assess the possible Hg remediation scenarios, hypothetical simulations were considered with the calibrated R-MCM.

B. Current Inputs

Results from R-MCM calibrated with current inputs of Hg_T and CH_3Hg^+ were compared to measurements made in previous studies of Hg in Onondaga Lake and to results from previous calibration of R-MCM by Gbondo-Tugbawa and Driscoll (1998) (Table 4.2.B). This was done in order to appraise the performance of the model in predicting concentrations of Hg_T and CH_3Hg^+. Concentrations of Hg_T and CH_3Hg^+ simulated by the model in the epilimnion, hypolimnion, and in fish lie with in the range of observed values from previous studies. Concentrations of Hg_T and CH_3Hg^+ obtained from model calibration were generally similar to values obtained by Gbondo-Tugwaba and Driscoll (1998). The exception for this pattern was evident in Hg concentrations in the hypolimnion. Concentrations of Hg in the hypolimnion simulated by this study (15.9 ng/L) were only one half of the value (29.5 ng/L) from Gbondo-Tugbawa and Driscoll (1998), while values of CH_3Hg^+ were much higher. This difference in simulated concentrations of Hg_T and CH_3Hg^+ in the hypolimnion could be explained by the increase particle deposition velocity used in these simulations in comparison to values used by Gbondo-Tugbawa and Driscoll (1998).

Table 4.2.B.A Comparison of model predicted concentrations of Hg in the water column, sediments and fish with previous studies of Onondaga Lake and previous model simulation.

Media	Species	Measured Values	R-MCM Gbondo-Tugbawa and Driscoll (1998)	This Study
Epilimnion (ng/L)	Hg^0	0.01-0.24	0.014	0.013
	CH_3Hg^+	0.2-2.0	0.5	0.33
	Hg_T	3.0-18.8	8.5	9.13
Hypolimnion (ng/L)	Hg^0	0.02-0.07	0.5	0.40
	CH_3Hg^+	0.4-21.7	3.1	7.72
	Hg_T	1.4-25.7	29.5	15.89
Sediments ($\mu g/g$)	CH_3Hg^+		0.14	0.39
	Hg_T	1.0-1.8	0.29	0.74
Smallmouth bass ($\mu g/g$)	Hg	0.95-1.4	1.0	1.02

The R-MCM was used to simulate mass fluxes of Hg_T and CH_3Hg^+ in the lake (Table 4.2.B.B). Fluxes of Hg_T and CH_3Hg^+ obtained from previous studies are also included in Table 4.2.B.B for comparison. The total input of Hg_T to the lake was 12.2 kg/year with the major tributaries, including METRO effluent, contributing about 81 %. Atmospheric deposition directly to the lake surface, which includes both dry and wet deposition, accounted for about 2.7 % of the input fluxes. Other inputs from minor tributaries and groundwater were estimated to contribute around 2.6 % of the input fluxes. The sinks of Hg_T include the lake outflow, volatilization and sediment burial. Outflow of Hg_T from the lake was estimated to be 7.56 kg/year (72 % of the Hg_T sinks), while 2.95 kg/year (28 % of the Hg_T sinks) was retained through the burial.

The major tributaries including METRO supplied 0.35 kg/year of CH_3Hg^+ to Onondaga Lake, about 16 % of the total inputs (2.13 kg/year). The major source of CH_3Hg^+ in the lake was net internal production (77 kg/year; 83 % of the total CH_3Hg^+ inputs). Atmospheric deposition and inputs from minor tributaries and groundwater were

minor sources contributing less than 0.5 % to the CH_3Hg^+ inputs of the lake. The major

sinks for CH_3Hg^+ in the lake were burial (1.55 kg/year; 72.6 % of the total CH_3Hg^+ sink)

and outflow (0.583 kg/year; 28.3 % of the total CH_3Hg^+ sink).

Table 4.2.B.B Comparison of mass balances of Hg_T and CH_3Hg^+ (kg/year) for
Onondaga Lake with measured results reported in previous studies and model
simulations with R-MCM.

Sources/Sinks	Measured Values		Gbondo-Tugbawa and Driscoll (1998)		This Study	
	Hg_T	CH_3Hg^+	Hg_T	CH_3Hg^+	Hg_T	CH_3Hg^+
Major Tributaries	6.0-13.15	0.26-0.45	9.50	0.31	9.90	0.35
Atmospheric Input	0.14		0.25	0.0024	0.33	0.002
Other Inflows			0.06	0.0024	0.32	0.007
Outflow	2.8 –6.17	0.24-0.39	6.17	0.39	7.56	0.58
Volatilization	0.15		0.002		0.0012	
Net methylation		0.63-1.01		1.76		1.77
Settling	48	1.92			24.03	11.61
Burial	47.7	0.199	1.83	1.59	2.94	1.55
Resuspension					12.7	6.74

These fluxes were compared with previous studies conducted in Onondaga Lake.

For the most part simulated values agreed with measured fluxes. Major discrepancies

between measured and model simulated values were evident for water column deposition

of Hg (48 vs. 24 kg/year for Hg_T and .92 vs. 1.6 kg/year for CH_3Hg^+) The lower

simulated value of Hg_T deposition to sediments compared to measured values could be

explained by the fact that measured values obtained from sediment traps represent

summer condition, when solids deposition is maximum. Indeed. Womble et al. (1996)

assumed that annual rates of solid deposition were about half of summer measured

values. In contrast. the very high rates of CH_3Hg^+ deposition to sediments simulated with

R-MCM are difficult to explain. Increased particle velocity could explain the difference

in burial rates between Gbondo-Tugbawa and Driscoll's study (1998) and this study. For

CH_3Hg^+, net methylation was the major source and sediment burial was the major sink.

In all mass balances, sedimentation rates (settling rates) were much higher than the total

inputs to the lake. This indicates that resuspension is a major mechanism of Hg supply to

the water column.

Hypolimnetic fluxes of TSS (3.7×10^7 and 5.7×10^5 kg/year for sedimentation

and mineralization, respectively, Table 4.2.B.C) simulated by the R-MCM were

compared with measured values (5.6×10^7 and 1.3×10^6 kg/year for sedimentation and

mineralization, respectively) in Onondaga Lake. The higher measured values of TSS

deposition to sediments compared to simulated values could be explained again by the

fact that measured values obtained from sediment traps represent summer condition,

when solids deposition is maximum. This discrepancy could explain the difference

between measured and simulated fluxes of Hg_T. These model calculations showed that

Hg deposition to the sediments largely depend on solids deposition in the lake since Hg

has a strong tendency to be associated with TSS. Also this study suggests that a great

portion of the settling fluxes are due to resuspened from sediments (approximately 90 %

and 80 % for the epilimnion and hypolimnion, respectively, Appendix VI).

Table 4.2.B.C Comparison of mass fluxes of TSS (kg/year) for Onondaga Lake with
measured results and model simulations with R-MCM.

	Settling	Burial	Resuspension	Mineralization
Measured values	5.6×10^7	4.0×10^7	N/A	1.3×10^6
Simulated values (hypolimnion)	3.7×10^7	6.8×10^6	3.0×10^7	5.4×10^5

C. Scenario Inputs

The effects of changing chemical and physical parameters on Hg concentrations in the epilimnion, hypolimnion, sediments and fish, and fluxes in the lake were investigated using the R-MCM. The fish species used in the simulation was smallmouth bass and Hg concentrations for five-year age class of smallmouth bass were reported. The various scenarios investigated were the following.

a) Hg Remediation Scenarios

Several scenarios of changes in direct reduction of Hg inputs were simulated. Current inputs (scenario   ) were compared to increased external inputs of Hg by 100 % (scenario 1.2) and reduced inputs of Hg by elimination of sources of Hg to the lake from METRO and leachate from the former chlor-alkali facilities (scenario 1.3, 1.4 and 1.5).

Results of the concentrations and fluxes for Hg remediation scenarios are given in Table 4.2.C.A.A, 4.2.C.A.B and 4.2.C.A.C.

Table 4.2.C.A.A Simulated concentrations of Hg in water (ng/L), sediments (μg/g) and fish (μg/g) in Onondaga Lake for the various scenarios considered.

| Scenario | Epilimnion | | | Hypolimnion | | | Sediments | | Fish |
	Hg^0	CH_3-Hg^+	Hg_T	Hg^0	CH_3-Hg^+	Hg_T	CH_3-Hg^+	Hg_T	CH_3-Hg^+
1.1	0.013	0.33	9.13	0.40	7.72	15.89	0.39	0.74	1.02
1.2	0.021	0.64	17.69	0.52	15.23	31.49	0.76	1.43	1.99
1.3	0.016	0.24	6.32	0.42	5.65	11.67	0.28	0.52	0.74
1.4	0.015	0.18	4.94	0.41	4.30	9.09	0.22	0.40	0.56
1.5	0.013	0.09	2.31	0.37	2.02	4.34	0.10	0.19	0.27

Doubling the tributary loads (scenario   2) resulted in increases, while reductions in tributary loads (scenario   3 to   5) resulted in decreases in Hg concentrations in the lake

water, sediments and fish. Because the model calculates steady-state values, and because water quality characteristics are assumed to remain constant, percentage increase and reduction in concentrations and fluxes predicted closely followed the percentage load increase and reduction. When inputs of Hg were doubled (scenario 1.2), concentrations of Hg in the water columns, sediments and fish were approximately doubled. When inputs from Ninemile Creek on the chlor-alkali leachate and METRO were eliminated (scenario 1.5), decreasing input fluxes of Hg_T and CH_3Hg^+ by 80 % and 50 %, respectively, the predicted concentrations of Hg_T and CH_3Hg^+ in the water column, sediments and fish were reduced by about 75 %. Similar patterns were observed in fluxes of Hg_T and CH_3Hg^+.

Table 4.2.C.A.B Major fluxes of Hg_T (kg/year) in Onondaga Lake for various scenarios considered.

Scenario	Inflow streams	Outflows	Settling	Burial	Resuspension
1.1	9.90	7.56	24.03	2.95	12.7
1.2	19.80	14.64	35.56	5.69	24.7
1.3	6.70	5.24	12.91	2.07	8.9
1.4	5.06	4.08	9.97	1.60	6.9
1.5	2.03	1.90	6.15	0.75	3.5

Results of these scenarios suggest that reduction of major inputs to Onondaga Lake could substantially reduce Hg concentrations in water column and fish. According to Gbonda-Tugbawa and Driscoll (1998), different sources of Hg_T to the lake likely exhibit different bioavailability (e.g., wastewater effluent vs. leachate from the former chlor-alkali facility). While these differences are undoubtedly important, they are not reflected in the model calculations.

Table 4.2.C.A.C Major fluxes of CH_3Hg^+ (kg/year) in Onondaga Lake for various scenarios considered.

Scenario	Inflow streams	Outflows	Settling	Burial	Net methylation	Resuspension
1.1	0.36	0.58	11.61	1.55	1.77	6.7
1.2	0.71	1.14	16.93	3.02	3.45	13.1
1.3	0.31	0.42	6.28	1.12	1.23	4.9
1.4	0.21	0.32	4.8	0.85	0.96	3.7
1.5	0.11	0.15	3.03	0.40	0.44	2.0

b) Effects of Changes in Allied Signal Activities

The closure of the chemical facility adjacent to Onondaga Lake has had profound effects on water quality. This perturbation may have consequences for biogeochemistry and bioavailability of Hg. Closure of the chemical facility has resulted in an approximately 0.5 pH increase in the water column of the lake due to decreases in precipitation of $CaCO_3$ (Driscoll et al., 1994) The closure also resulted in marked decreases in Cl^- concentrations (Driscoll et al., 1994). Chloride is an important complexing ligand of Hg. The effects of changes in Cl^- were examined by a 50 % increase (scenario 2.3), a 10 % decrease (scenario 2.4), a 20 % decrease (scenario 2.5) and a 50 % decrease (scenario 2.6) in water column Cl^- concentrations. Finally decreases in Ca load to the lake resulted in decreases in the formation of $CaCO_3$. This coincided with decreases in rates of particle deposition in the water column (Womble et al. 1995). This effect was simulated by decreasing (scenario 2.7) and increasing (scenario 2.8) the particle settling velocity in the lake by 50 %. These hypothetical conditions were compared to the calibrated model (scenario 2.

The model results of the concentrations and fluxes for these hypothetical changes resulted from changes in the lake due to the chemical facility are given in Table

4.2.C.B.A, 4.2.C.B.B and 4.2.C.B.C. When pH increased by 0.5 in the water column (scenario 2.2), Hg concentrations in fish decreased 2% and concentrations of CH_3Hg^+ increased about 55 % in the epilimnion and about 60 % in the hypolimnion. Increased reduction of Hg_T^{2+} in neutral pH lakewaters may be an important mechanism for decreasing the supply of substrate for in-lake methylation (Fitzgerald et al, 1991). The results from scenario 2.2 confirm that reduction is a highly pH-dependent process. Concentrations of Hg_T^{2+} decreased with higher pH, while concentrations of CH_3Hg^+ increased.

Table 4.2.C.B.A Simulated concentrations of Hg in water (ng/L), sediments (μg/g) and fish (μg/g) in Onondaga Lake for the various scenarios considered.

| Scenario | Epilimnion | | | Hypolimnion | | | Sediments | | Fish |
	Hg^0	CH_3-Hg^+	Hg_T	Hg^0	CH_3-Hg^+	Hg_T	CH_3-Hg^+	Hg_T	CH_3-Hg^+
2.1	0.013	0.33	9.13	0.40	7.72	15.89	0.39	0.74	1.02
2.2	0.014	0.51	9.01	0.41	12.48	17.97	0.33	0.76	1.00
2.3	0.015	0.28	9.88	0.42	6.67	15.85	0.43	0.62	1.09
2.4	0.013	0.34	8.90	0.40	7.98	15.65	0.38	0.78	1.00
2.5	0.014	0.35	8.64	0.40	8.27	15.40	0.36	0.82	0.97
2.6	0.014	0.39	7.61	0.41	9.34	14.44	0.30	1.00	0.87
2.7	0.013	0.53	10.03	0.40	6.28	11.96	0.31	0.52	1.08
2.8	0.017	0.24	8.44	0.46	8.47	19.20	0.43	0.90	0.95

Since Hg_T^{2+} is the substrate for methylation, the effects of reduction on CH_3Hg^+ concentrations roughly parallel the Hg_T^{2+} variations (Watras and Huckabee, 1994). Thus reduction should be a major contributor to decreases in fish Hg. Other than the concentrations of Hg_T^{2+} and CH_3Hg^+ in the water column and fish, changes in pH did not affect model simulations when compared to values from scenario 2 (current inputs).

Table 4.2.C.B.B Major fluxes of Hg_T (kg/year) in Onondaga Lake for various scenarios considered.

Scenario	Inflow streams	Outflows	Settling	Burial	Resuspension
2.1	9.9	7.56	24.03	2.95	12.7
2.2	9.9	7.48	24.98	3.02	13.0
2.3	9.9	8.06	14.69	2.45	10.6
2.4	9.9	7.40	25.09	3.09	13.4
2.5	9.9	7.22	26.28	3.27	14.1
2.6	9.9	6.52	30.87	3.95	17.1
2.7	9.9	8.46	8.95	2.04	3.3
2.8	9.9	6.91	32.36	3.58	25.2

Changes in Cl^- concentrations altered concentrations and transfers of Hg, because Cl^- complexes Hg and uptake of CH_3Hg^+ in phytoplankton is a function of the species associated with inorganic complexes in the water column (scenarios 2.3 – 2.6). As Cl^- concentrations decreased, concentrations of CH_3Hg^+ in the water column, settling flux of Hg_T and burial flux of Hg_T increased, while the concentrations in fish, concentrations of Hg_T in the water column, settling flux of CH_3Hg^+ and the outflow fluxes of Hg_T and CH_3Hg^+ decreased. This analysis suggests that the increase in fish Hg concentrations immediately following the closure of the soda ash manufacturing facility was probably not due to decreases in Cl^- concentrations in the lake

Table 4.2.C.B.C Major fluxes of CH_3Hg^+ (kg/year) in Onondaga Lake for various scenarios considered.

Scenario	Inflow streams	Outflows	Settling	Burial	Net methylation	Resuspension
2.1	0.36	0.58	11.61	1.55	1.77	6.7
2.2	0.36	0.71	9.60	1.30	1.65	5.7
2.3	0.36	0.57	9.59	1.70	1.91	7.4
2.4	0.36	0.58	11.22	1.49	1.71	6.6
2.5	0.36	0.58	10.79	1.43	1.64	6.3
2.6	0.36	0.58	9.16	1.18	1.39	5.5
2.7	0.36	0.93	4.72	1.23	1.80	2.0
2.8	0.36	0.42	14.12	1.70	1.96	12.0

Changes in particle velocity altered concentrations and fluxes of Hg_T and CH_3Hg^+ in the lake. When particle velocity decreased (scenario 2.7), concentrations of Hg in the epilimnion increased and outflow flux increased because there are more suspended particles associated with Hg in the epilimnion when compared to the reference scenario 2.1. In contrast, concentrations of Hg in the hypolimnion increased as particle velocity increased (scenario 2.8). Settling and burial fluxes also increased due to increased settling velocity.

Changes in particle settling velocity also altered fluxes of TSS in the lake (Table 4.2.C.B.D). When particle settling velocity decreased (scenario 2.7), settling and resuspension fluxes decreased in the epilimnion and hypolimnion, compared to calibrated values (scenario 2.1). These decreased TSS fluxes would explain the simulated increases of Hg concentrations in the water column and fish. Increased fluxes of settling and resuspension were also simulated with increased particle velocity (scenario 2.8) in the water columns. When TSS fluxes were increased, decreased Hg concentrations in the water column and fish were simulated by R-MCM.

Table 4.2.C.B.D Major fluxes of TSS (kg/year) in Onondaga Lake (hypolimnion) for various scenarios considered.

	Settling	Burial	Resuspension	Mineralization
2.1	3.7×10^7	6.8×10^6	3.0×10^7	5.4×10^5
2.7	1.9×10^7	6.8×10^6	1.1×10^7	5.4×10^5
2.8	5.6×10^7	6.8×10^6	4.9×10^7	5.4×10^5

c) Effects of Changing in METRO and TSS Inputs to the Lake

Finally model calculations were conducted to evaluate the effects of METRO inputs and other processes regulating TSS inputs to the lake. Discharge of phosphorus from METRO results in the production of phytoplankton. This increases concentrations of solids in the lake. Simulations were conducted increasing (scenario 3.2) and decreasing (scenario 3.3). Total suspended solids concentrations in the lake were used to depict changes in phosphorus loading. Also a simulation was conducted to eliminate the external inputs of TSS to the lake (scenario 3.4). This calculation might depict the effects of watershed control of TSS inputs (e.g. solids control of the Tully mudboils). These simulations were compared to results from the reference simulation (scenario 3.1).

Results of the concentrations and fluxes for these scenarios are given in Table 4.2.C.C.A, 4.2.C.C.B and 4.2.C.C.C

Table 4.2.C.C.A Simulated concentrations of Hg in water (ng/L), sediments (μg/g) and fish (μg/g) in Onondaga Lake for the various scenarios considered.

Scenario	Epilimnion			Hypolimnion			Sediments		Fish
	Hg^0	CH_3-Hg^+	Hg_T	Hg^0	CH_3-Hg^+	Hg_T	CH_3-Hg^+	Hg_T	CH_3-Hg^+
3.1	0.013	0.33	9.13	0.40	7.72	15.89	0.39	0.74	1.02
3.2	0.017	0.20	8.04	0.45	6.54	16.32	0.33	0.77	0.85
3.3	0.017	0.40	9.50	0.45	13.25	24.33	0.65	1.08	1.13
3.4	0.018	0.57	10.87	0.50	18.47	29.70	0.89	1.26	1.29

When TSS were increased by 50 % (scenario 3.2), concentrations of Hg in water column and fish decreased because a larger amount of Hg is associated with suspended solids and settle into the sediments. Therefore, settling and burial fluxes of Hg increased.

As concentrations of TSS decreased in the water column, concentrations of Hg in waters increased. Methylation also increased due to decreased TSS in the water column. Increased in the rates of methylation contributed to increases in fish Hg.

Table 4.2.C.C.B Major fluxes of Hg_T (kg/year) in Onondaga Lake for various scenarios considered.

Scenario	Inflow streams	Outflows	Settling	Burial	Resuspension
3.1	9.90	7.56	24.03	2.95	12.7
3.2	9.90	7.06	30.98	3.43	22.0
3.3	9.90	7.87	22.67	2.63	16.5
3.4	9.90	8.38	9.26	1.35	11.8

This analysis suggest that the increase in fish Hg concentrations immediately following the closure of Allied Signal Inc. was probably due to decreases in TSS concentrations in the lake. In the steady-state R-MCM, methylation rates are proportional to Hg_T^{2+}, which causes the specific methylation rate to be independent of pH (Watras and Huckabee. 1994).

Table 4.2.C.C.C Major fluxes of CH_3Hg^+ (kg/year) in Onondaga Lake for various scenarios considered.

Scenario	Inflow streams	Outflows	Settling	Burial	Net methylation	Resuspension
3.1	0.36	0.58	11.61	1.55	1.77	6.7
3.2	0.36	0.47	13.61	1.64	1.75	10.1
3.3	0.36	0.69	12.24	1.58	1.90	9.9
3.4	0.36	0.93	11.35	1.42	2.00	8.4

Changes in TSS concentrations in the water column also affected simulated fluxes of TSS in Onondaga Lake (Table 4.2.C.C.D). When TSS concentrations increased

(scenario 3.2), all TSS fluxes (settling, burial, resuspension and mineralization) increased in the epilimnion and hypolimnion, compared to calibrated values (scenario 3.1). In contrast, decreased TSS fluxes were simulated following decreases in TSS concentrations (scenario 3.3 and 3.4). These changes in TSS fluxes could explain the changes in concentrations of Hg in the water column, sediments and fish in Onondaga Lake. When higher TSS concentrations were simulated, the increases in TSS fluxes resulted in lower concentrations of Hg in the water column and fish in simulations by R-MCM.

Table 4.2.C.C.D Major fluxes of TSS (kg/year) in Onondaga Lake (hypolimnion) for various scenarios considered.

	Settling	Burial	Resuspension	Mineralization
3.1	3.7×10^7	6.8×10^6	3.0×10^7	5.4×10^5
3.2	5.6×10^7	7.7×10^6	4.8×10^7	5.4×10^5
3.3	3.1×10^7	4.3×10^6	2.6×10^7	3.6×10^5
3.4	1.9×10^7	2.5×10^6	1.6×10^7	1.8×10^5

4.3 Summary

The pattern that emerges from this analysis is that the Hg biogeochemistry of Onondaga Lake is strongly controled by particle dynamics and the highly reducing conditions that occur in the lower waters during summer stratification. Although there are currently modest inputs of Hg to Onondaga Lake (largely from the site of the former chlor-alkali facility and METRO), the supply of Hg to the water column of Onondaga Lake appears to be largely from derived from sediments. There is considerable evidence to support this contention. including) mass balance calculations which show internal fluxes of Hg in sediment traps and burial fluxes of Hg to the lake, 2) the Hg content of particulate matter increased markedly from tributary waters (0. – 0.4 µg/g) to the lake

itself (1.3 – 2.8 μg/g) indicating internal source of Hg to the lake and 3) model simulations. The large internal production of particles enhances Hg deposition to sediments and in-lake retention of Hg. Mass balance calculations suggest that approximately 80 % of the inputs of Hg_T are retained in the lake.

The other distinguishing feature of Hg dynamics in Onondaga lake is the very high rates of CH_3Hg^+ production among the highest values reported in the literature. High rates of methylation of Hg in Onondaga lake are undoubtedly due to several factors: 1) the high supply of Hg_T^{2+} associated with particulate matter depositing to the hypolimnion, 2) very high inputs of labile organic matter to the hypolimnion which fuels microbial methylation and 3) highly reducing conditions which promotes populations of sulfate reducing bacteria which largely mediate methylation of Hg_T

Despite the elevated supply of Hg_T^{2+} and very high rates of methylation, fish Hg concentrations are not abnormally high in Onondaga Lake. Indeed, given the characteristics of the lake (i.e. high inputs of Hg_T^{2+} and high rates of methylation), it is somewhat surprising that fish Hg concentrations are not higher. Concentrations of Hg in fish tissue in Onondaga Lake are similar to values reported for fish in remote lakes imported by atmospheric Hg deposition (Grieb et al., 1989; Driscoll et al 1995). The BCF of CH_3Hg^+ is not abnormally high, values are similar to those reported for the fish studies (Driscoll et al., 1994) This suggests that other factors mitigate against the bioaccumulation of Hg in biological tissue In Onondaga Lake these factors would appear to be high concentrations of particulate matter and sulfide. R-MCM simulations demonstrate that high rates of particulate matter deposition decrease the bioavailability of Hg for methylation and the subsequent uptake of CH_3Hg^+ in aquatic biota. Indeed,

partition coefficients of Hg by particulate matter calculated for Onondaga lake are similar to values reported for other systems. However, the high production of TSS appears to diminish the CH_3Hg^+ accumulation in fish. Onondaga Lake is also characterized by high concentrations of sulfide in the hypolimnion during summer stratification (Wang and Driscoll, 1995; Effler et al., 1996). Due to the strong binding of Hg for sulfide it seems likely that sulfides also reduce the bioavalability of Hg.

These patterns have implications for the remediation of Hg contamination in the lake. Model simulations suggest that decreases in external loading of Hg will ultimately reduce water column, sediments and fish Hg concentrations. However, the effects of reduced loading are attenuated by the large rate of production and deposition of particulate matter in the lake which promotes in-lake retention and cycling. This effect is supported by the long period over which elevated fish Hg concentrations have been observed following closure of the chlor-alkali facility. It would seem that dredging is the only management option which could result in marked reductions in fish Hg concentrations over a short period. The difficulty in dredging is because 28 years after closure of the chlor-alkali facility much of the Hg has been buried in sediments (Rowell. 1996). Dredging would require deep excavation of sediments resulting in an expensive operation and rushing the mobilization of Hg.

Note that any management of the lake which alters the productivity and/or particle production will alter fish Hg concentrations. Model simulations suggest that the large increase on concentrations of Hg in smallmouth bass in the late 1980's following closure of the soda ash facility was due to decreases in particulate deposition and/or concentrations in the lake. Reduction in the lake productivity that is planned over the

next 15 years in response to Onondaga County's Municipal Compliance Plan may affect the Hg dynamics of the lake. Diminished particulate production should enhance Hg transport to the outlet of the lake and decrease Hg transport to sediments. Anticipated decreased in TSS concentrations should enhance the rates of methylation and the bioavalability of Hg. However, decreases in lake productivity should diminish hypolimnetic depletion of oxygen and rates of methylation. The effects of these changes would be difficult to predict.

Chapter 5 - Conclusions

Based on the mass balances of Hg_T and CH_3Hg^+, the empirical relationships between Hg and TSS, the observed distribution of Hg in aquatic food chain and various R-MCM calculations for Onondaga Lake, several conclusions could be made.

- Fluxes of Hg_T from resuspension and deposition to sediments ($\approx$ 50 kg/year) were much larger than external fluxes of Hg ($\approx$ 10 kg/year). This pattern suggests much of the ongoing elevated concentrations of Hg in the lake is due to Hg contamination in sediments.

- Internal production (1.01 kg/year) (methylation and flux from sediments) was a major source of CH_3Hg^+ to Onondaga Lake with values much greater than external fluxes of CH_3Hg^+ (0.45 kg/year). Values of CH_3Hg^+ production in Onondaga Lake are among the highest values reported in the literature

- A large amount of TSS (83 %) supplied to the lake was associated with in-lake production.

- There was a marked increase in the Hg content of particulate matter from the tributaries to Onondaga Lake (0. µg/g to 0.4 µg/g), to the water column particles (2.8 µg/g), sedimenting particles   3 µg/g) and surface sediments (1.8 µg/g) This increase is suggestive of an internal source of Hg to the lake.

- The analysis of Hg_T occurring as CH_3Hg^+ in aquatic species of Onondaga Lake confirms that CH_3Hg^+ is more efficiently transferred to higher levels of aquatic food web than Hg^{2-}

- Concentrations of CH_3Hg^+ and bioconcentration factors (BCFs) of CH_3Hg^+ increased with increasing trophic levels in aquatic food chain of Onondaga Lake

- R-MCM simulations demonstrated a decrease in the concentrations of particulate matter may decrease the bioavailability of Hg for methylation and the subsequent uptake of CH_3Hg^+ in aquatic biota.

- Model simulations suggest that decreases in external loading of Hg will ultimately reduce water column, sediments and fish Hg concentrations.

- Model simulations suggest that the large increase on concentrations of Hg in smallmouth bass in the late 1980's following closure of the soda ash facility be due to decreases in particulate deposition and/or concentrations in the lake.

- Model calculations showed that the large internal production of particles enhances Hg deposition to sediments and in-lake retention of Hg.

Chapter 6 - Suggestions for Future Research

1. A more accurate mass balances of Hg_T and CH_3Hg^+ should be obtained through future research. The north and south basins of Onondaga Lake probably contain different amounts of Hg in the sediments and in the water column. The south basin receives Hg loadings from METRO, Onondaga Creek, Ley Creek and Harbor Brook, while the north basin receives Hg from Ninemile Creek. The north basin also contains the lake outlet. Studying the effect of the different inputs on the individual basins would provide a more complete picture of the Hg cycle in Onondaga Lake.

2. Future studies on Hg should be planned to monitor the concentrations of Hg at closer time intervals. Increasing the number of samples collected will reduce uncertainties in order to have a more accurate Hg budget for Onondaga Lake

3. Meaningful correlations should be obtained if concentrations of auxiliary parameters (e.g. TSS, SO_4^{2-}, DO, DOC and pH) are monitored when Hg concentrations are monitored. Correlations between Hg and other parameters would provide better understanding of biogeochemistry of Hg in Onondaga Lake.

4. Expand the hydrodynamic model for the lake outlet to include Onondaga Lake and Seneca River. The expanded hydrodynamic model would provide better understanding of Hg cycle in the lake.

Appendix I

Concentrations (ng/L) of Hg_T in south basin of Onondaga Lake for the period April to November 1992 (after Jacobs et al., 1995)

Date	Depth (m)	Total Hg_T	Dissolved Hg_T	Particulate Hg_T
	0		2.30	2.70
	0		1.40	1.60
	0		1.30	2.40
	0		4.20	2.70
	0		2.40	3.80
				7.40
				0.70
				2.50
				4.30
				2.90
				2.40
				3.40
				4.90
			2.	
			1.	
			1.	
			3.	
			2.	

Jun-92	18	7.00	4.10	2.90
Jul-92	18	13.80	3.70	10.10
Aug-92	18	18.00	8.50	9.50
Sep-92	18	22.70	7.10	15.60

Concentrations (ng/L) of Hg_T in north basin of Onondaga Lake for for the period April to November 1992 (after Jacobs et al., 1995)

Date	(m) Depth	(ng/L) Total Hg_T	(ng/L) Dissolved Hg_T	(ng/L) Particulate Hg_T
	0	3.00	1.70	1.30
	0	5.00	1.80	3.20
	0	3.00	1.80	1.20
	0	4.80	1.40	3.40
	0	11.20	4.10	7.10
	0	6.90	2.50	4.40
	3	4.00	1.90	2.10
	3	3.00	1.80	1.20
	3	3.40	1.30	2.10
	3	7.00	5.40	1.60
	3	7.70	3.00	4.70
	3	5.00	2.40	2.60
	3	7.40	2.70	4.70
May-92	6	4.00	1.80	2.20
Jun-92	6	3.00	2.00	1.00
Jul-92	6	6.20	0.65	5.55
Aug-92	6	4.70	3.20	1.50
Sep-92	6	5.30	2.60	2.70
Apr-92	9	7.00	4.10	2.90
May-92	9	3.00	1.50	1.50
Jun-92	9	4.00	1.90	2.10
Jul-92	9	5.40	1.80	3.60
Aug-92	9	5.30	3.70	1.60
Sep-92	9	5.10	3.10	2.00
Oct-92	9	4.50	2.00	2.50
Nov-92	9	5.30	2.30	3.00
May-92	12	5.00	1.60	3.40
Jun-92	12	6.00	2.30	3.70
Jul-92	12	7.40	3.00	4.40
Aug-92	12	15.20	5.70	9.50
Sep-92	12	18.60	6.20	12.40
Apr-92	15	6.00	2.80	3.20
May-92	15	5.00	2.20	2.80
Jun-92	15	6.00	4.60	1.40
Aug-92	15	18.30	9.80	8.50
Sep-92	15	19.70	8.90	10.80
Oct-92	15	22.50	10.70	11.80
Nov-92	15	5.40	2.20	3.20
May-92	18	6.00	2.10	3.90

Jun-92	18	80	4.20	3.60
Jul-92	18	13.20	3.60	9.60
Aug-92	18	16.10	8.70	7.40
Sep-92	**18**	**20.60**	**8.80**	**11.80**

Concentrations (ng/L) of CH_3Hg^+ in south basin of Onondaga Lake for the period April to November 1992 (Jacobs et al., 1995)

Date	Depth (m)	Total CH_3Hg^+	Dissolved CH_3Hg^+	particulate CH_3Hg^+
May-92	0	0.22	0.08	0.14
Jun-92	0	0.43	0.16	0.27
Jul-92	0	0.33	0.06	0.27
Aug-92	0	0.33	0.07	0.26
Sep-92	0	0.33	0.21	0.12
Apr-92	3	0.25	0.09	0.17
May-92	3	0.37	0.15	0.22
Jun-92	3	0.40	0.17	0.23
Jul-92	3	0.34	0.09	0.26
Aug-92	3	0.29	0.07	0.22
Sep-92	3	0.57	0.23	0.34
Oct-92	3	1.70	0.43	1.27
Nov-92	3	1.30	0.68	0.62
?-92	6	0.14	0.11	0.03
	6	0.38	0.17	0.21
	6	0.25	0.09	0.16
?	6	0.18	0.10	0.08
Sep-92	6	0.43	0.21	0.22
Apr-92	9	0.43	0.10	0.33
May-92	9	0.24	0.08	0.16
Jun-92	9	1.10	0.47	0.63
Jul-92	9	0.45	0.23	0.22
Aug-92	9	0.69	0.33	0.36
Sep-92	9	0.53	0.19	0.34
Oct-92	9	1.10	0.45	0.65
Nov-92	9	1.40	0.82	0.58
?-92	12	0.29	0.13	0.16
	12	1.10	1.00	0.10
	12	3.60	2.10	1.50
?	12	8.60	4.10	4.50
Sep-92	12	5.30	3.60	1.70
Apr-92	15	0.39	0.12	0.27
May-92	15	0.81	0.22	0.59
Jun-92	15	3.70	2.20	1.50
Jul-92	15	7.60	1.70	5.90
Aug-92	15	10.60	3.40	7.20
Nov-92	15	1.50	0.43	1.07
?-92	18	1.10	0.35	0.75

Jun-92		40	**3.**60	2.80
Jul-92	18	7.20	2.40	4.80
Aug-92	**18**	**7.00**	**3.50**	**3.50**
Sep-92	**18**	**5.20**	**3.20**	**2.00**

Concentrations (ng/L) of CH_3Hg^+ in north basin of Onondaga Lake for the period April to November 1992 (Jacobs et al., 1995)

Date	(m) Depth	(ng/L) Total CH_3Hg^+	(ng/L) Dissolved CH_3Hg^+	(ng/L) particulate CH_3Hg^+
May-92	0	2.00	0.22	1.78
May-92	0	0.20	0.04	0.16
Jun-92	0	0.32	0.14	0.18
Jul-92	0	0.37	0.09	0.28
Aug-92	0	0.16	0.07	0.10
Sep-92	0	0.26	0.04	0.22
May-92	3	0.38	0.06	0.32
Jun-92	3	0.35	0.14	0.21
Jul-92	3	0.32	0.06	0.26
Aug-92	3	0.31	0.04	0.27
Sep-92	3	0.47	0.11	0.36
Oct-92	3	1.30	0.31	0.99
Nov-92	3	1.60	0.86	0.74
May-92	6	0.18	0.09	0.09
Jun-92	6	0.37	0.18	0.19
Jul-92	6	0.29	0.09	0.20
Aug-92	6	0.18	0.10	0.08
Sep-92	6	0.44	0.12	0.32
Apr-92	9	0.31	0.13	0.18
May-92	9	0.45	0.10	0.35
Jun-92	9	0.94	0.41	0.53
Jul-92	9	0.59	0.23	0.36
Aug-92	9	0.39	0.20	0.19
Sep-92	9	1.00	0.38	0.62
Oct-92	9	0.66	0.33	0.33
Nov-92	9	1.40	0.75	0.65
May-92	12	0.37	0.04	0.33
Jun-92	12	2.50	1.40	1.10
Jul-92	12	3.20	1.70	1.50
Aug-92	12	7.40	2.70	4.70
Sep-92	12	10.50	3.40	7.10

Jun-92		4.70	3.40	1.30
Jul-92	18	6.40	3.60	2.80
Aug-92	18	6.30	4.00	2.30
Sep-92	18	7.00	4.00	3.00

Concentrations (ng/L) of Hg_T^{2+} in south basin of Onondaga Lake for the period April to November 1992 (Jacobs et al., 1995)

Date	Depth (m)	Total Hg_T^{2+}	Dissolved Hg_T^{2+}	Particulate Hg_T^{2+}
	0	4.78	2.22	2.56
	0	2.57	1.24	1.33
	0	3.37	1.24	2.13
	0	6.57	4.13	2.44
	0	5.87	2.19	3.68
	3	9.75	2.52	7.24
	3	2.63	2.15	0.48
	3	4.60	2.33	2.27
	3	5.66	1.62	4.05
	3	6.41	3.73	2.68
	3	5.33	3.27	2.06
	3	3.70	1.57	2.13
	3	6.00	1.72	4.28
		2.86	1.99	0.87
		2.62	0.93	1.69
		5.35	1.31	4.04
		5.62	3.20	2.42
		6.77	2.69	4.08
Apr-92	9	11.57	3.40	8.17
May-92	9	2.76	1.52	1.24
Jun-92	9	1.90	1.13	0.77
Jul-92	9	3.35	1.17	2.18
Aug-92	9	4.71	3.27	1.44
Sep-92	9	7.87	2.51	5.36
Oct-92	9	4.00	1.95	2.05
Nov-92	9	4.10	2.48	1.62
May-92	12	4.71	2.27	2.44
Jun-92	12	1.90	1.10	0.80
Jul-92	12	4.60	1.10	3.50
Aug-92	12	10.20	2.30	7.90
Sep-92	12	13.70	1.70	12.00
Apr-92	15	28.61	4.08	24.53
May-92	15	3.19	1.68	1.51
Jun-92	15	5.30	1.20	4.10
Jul-92	15	7.00	2.20	4.80
Aug-92	15	7.10	4.40	2.70
Nov-92	15	4.60	2.17	2.43
May-92	18	4.90	2.15	2.75

Jun-92	18	0.60	0.50	0.10
Jul-92		6.60	1.30	5.30
Aug-92	18	11.00	5.00	6.00
Sep-92	18	17.50	3.90	13.60

Concentrations (ng/L) of Hg_T^{2+} in north basin of Onondaga Lake for the period April to November 1992 (Jacobs et al., 1995)

Date	Depth (m)	Total Hg_T^{2+}	Dissolved Hg_T^{2+}	Particulate Hg_T^{2+}
May-92	0	1.00	1.48	-0.48
May-92	0	4.80	1.76	3.04
Jun-92	0	2.68	1.66	1.02
Jul-92	0	4.43	1.31	3.12
Aug-92	0	11.04	4.04	7.01
Sep-92	0	6.64	2.46	4.18
May-92	3	3.62	1.84	1.78
Jun-92	3	2.65	1.66	0.99
Jul-92	3	3.08	1.24	1.84
Aug-92	3	6.69	5.36	1.33
Sep-92	3	7.23	2.89	4.34
Oct-92	3	3.70	2.09	1.61
Nov-92	3	5.80	1.84	3.96
May-92	6	3.82	1.71	2.11
Jun-92	6	2.63	1.82	0.81
Jul-92	6	5.91	0.56	5.35
Aug-92	6	4.52	3.10	1.42
Sep-92	6	4.86	2.48	2.38
Apr-92	9	6.69	3.97	2.72
May-92	9	2.55	1.40	1.15
Jun-92	9	3.06	1.49	1.57
Jul-92	9	4.81	1.57	3.24
Aug-92	9	4.91	3.50	1.41
Sep-92	9	4.10	2.72	1.38
Oct-92	9	3.84	1.67	2.17
Nov-92	9	3.90	1.55	2.35
May-92	12	4.63	1.56	3.07
Jun-92	12	3.50	0.90	2.60
Jul-92	12	4.20	1.30	2.90
Aug-92	12	7.80	3.00	4.80
Sep-92	12	8.10	2.80	5.30
Apr-92	15	5.68	2.66	3.02
May-92	15	3.80	1.86	1.94
Jun-92	15	2.30	1.90	0.40
Aug-92	15	10.50	6.40	4.10
Sep-92	15	9.10	3.80	5.30
Oct-92	15	10.10	1.50	8.60
Nov-92	15	4.20	1.60	2.60
	18	4.40	1.66	2.74

Jun-92	18		0.80	2.30
Jul-92	18	6.80	0.00	6.80
Aug-92	18	9.80	4.70	5.10
Sep-92	18	13.60	4.80	8.80

Appendix II

Concentrations of TSS (mg/L) in Onondaga Lake for the period of April to October 1995 (after UFI, unpublished data)

Depth (m)\Date	4/7/95	4/13/95	4/21/95	4/28/95
0	2.80	2.50	2.35	3.10
4	2.20	3.33	3.73	4.60
8	2.87	2.27	3.87	1.87
12	2.60	2.40	1.80	1.33
16	2.20	2.00	0.93	0.93

Depth (m)\Date	5/5/95	5/12/95	5/19/95	5/26/95
0	0.85	0.51	0.23	0.27
4	1.67	0.77	1.30	0.83
8	1.15	0.89	1.20	0.63
12	51.55	0.99	1.30	0.53
16	1.13	1.27	1.15	0.60

Depth (m)\Date	6/2/95	6/9/95	6/16/95	6/23/95	6/30/95
0	0.40	0.74	2.75	10.29	3.37
4	0.70	0.97	1.10	9.50	7.50
8	0.17	1.03	0.97	1.27	3.90
12	0.43	0.93	0.80	1.33	1.55
16	0.87	0.87	1.00	1.00	0.90

Depth (m)\Date	7/7/95	7/21/95	7/28/95
0	3.67	2.60	3.90
4	2.95	3.73	7.40
8	2.85	1.53	1.67
12	1.80	1.47	2.53
16	1.70	0.73	1.53

Depth (m)\Date	8/4/95	8/11/95	8/18/95	8/25/95
0	3.87	3.00	3.08	3.67
4	2.73	2.67	3.80	3.80
8	1.85	2.07	2.06	3.93
12	0.95	0.75	1.20	1.20
16	1.60	1.00	1.23	0.75

Depth (m)\Date	9/1/95	9/8/95	9/15/95	9/21/95	9/29/95
0	3.93	4.27	3.14	3.27	3.87
4	3.10	4.40	3.09	3.53	3.15
8	4.10	4.91	3.26	4.13	3.15
12	1.00	1.53	1.00	2.53	1.30
16	0.50	N/A	1.30	1.67	0.70

Depth (m)\Date	10/6/95	10/13/95	10/20/95	10/27/95
0	3.04	3.30	3.93	7.20
4	3.12	3.80	4.20	4.06
8	3.52	2.00	3.87	4.56
12	1.40	2.10	4.80	4.87
16	0.73	1.20	1.20	4.40

Appendix III

Gross sedimentation rate for Hg$_T$, CH$_3$Hg$^+$ and TSS for the period of June to November 1992
(after PTI Environmental Service, 1997)

Month	Hg$_T$ (μg/m^2-day)		CH$_3$Hg$^+$ (μg/m^2-day)		TSS (g/m^2-day)	
	South Basin	North Basin	South Basin	North Basin	South Basin	North Basin
Jun	4.87	N/A	0.25	N/A	8.880	N/A
July	17.79	14.38	0.86	0.76	10.151	10.828
Aug	13.38	9.65	0.86	0.64	14.057	12.102
Sep	20.70	9.62	0.71	0.53	9.283	8.151
Oct	12.63	7.56	0.45	0.35	6.476	5.289
Nov	N/A	6.61	N/A	0.80	N/A	5.049

N/A = sample not collcted

Appendix IV

Concentrations of Hg_T (ng/L) for the period October 1995 -
September 1996 (after Gbondo-Tugbawa et al., 1998)

	Ninemile Creek	Onondaga Creek	Harbor Brook	Ley Creek	METRO
10/18/95	22.44	7.72	6.39	4.01	28.36
11/28/95	17.85	7.33	7.07	3.80	46.53
12/18/95	12.31	5.35	4.28	3.61	14.03
1/30/96	13.97	5.01	5.15	4.17	42.30
2/29/96	11.68	6.13	5.05	5.56	44.47
3/6/96	15.11	7.41	N/A	N/A	N/A
3/13/96	10.56	6.78	N/A	N/A	N/A
3/20/96	13.55	9.23	N/A	N/A	N/A
3/28/96	12.66	7.42	6.44	6.14	27.90
4/29/96	11.55	8.16	10.44	6.03	65.57
5/30/96	24.56	10.89	8.65	9.01	7.07
6/27/96	35.83	11.52	7.89	9.52	66.67
7/25/96	31.83	14.52	5.60	5.38	15.30
8/29/96	16.23	7.85	4.21	4.36	12.24
9/19/96	18.66	8.38	4.88	8.48	6.63

Concentrations of CH_3Hg^+ (ng/L) for the period October 1995
September 1996 (after Gbondo-Tugbawa et al., 1998)

	Ninemile Creek	Onondaga Creek	Harbor Brook	Ley Creek	METRO
10/18/95	0.55	0.35	0.45	0.37	1.45
11/28/95	0.40	0.20	0.49	0.22	0.78
12/18/95	0.24	0.37	0.41	0.28	0.63
1/30/96	0.28	0.17	0.38	0.31	2.40
2/29/96	0.39	0.43	0.40	0.34	1.79
3/6/96	0.34	0.40	N/A	N/A	N/A
3/13/96	0.31	0.43	N/A	N/A	N/A
3/20/96	0.41	0.49	N/A	N/A	N/A
3/28/96	0.22	0.42	0.87	0.62	1.73
4/29/96	0.41	0.43	1.49	0.43	1.26
5/30/96	0.73	0.51	0.58	0.51	3.70
6/27/96	1.42	0.77	0.52	0.65	2.07
7/25/96	1.10	0.97	0.32	0.37	0.69
8/29/96	0.56	0.51	0.51	0.28	0.92
9/19/96	0.49	0.36	0.62	0.47	0.67

Appendix V

Concentrations of Hg in white perch for the period of 1973 to 1992
(R. Sloan, NYS Department of Environmental Conservation, unpublished data)

Year	Age	Hg (µg/g)	Year	Age	Hg (µg/g)
1973	4.0	0.81	1981	6.0	0.97
1973	5.0	1.04	1981	7.0	0.99
1973	6.0	1.30	1981	8.0	0.91
1973	7.0	1.75	1981	9.0	1.04
1973	8.0	1.72	1992	3.0	1.20
1973	9.0	2.47	1992	4.0	1.04
1974	4.0	0.20	1992	5.0	1.16
1974	5.0	0.26			
1974	6.0	0.27			
1974	7.0	0.71			
1974	8.0	0.64			
1974	9.0	1.12			
1974	10.0	1.94			
1975	3.0	1.20			
1975	4.0	1.21			
1975	5.0	1.27			
1975	6.0	1.32			
1975	7.0	1.71			
1975	8.0	1.56			
1975	9.0	2.19			
1975	10.0	2.17			
1976	2.0	0.35			
1976	3.0	0.60			
1976	4.0	0.57			
1976	5.0	0.83			
1976	6.0	0.85			
1976	7.0	0.85			
1976	8.0	0.76			
1976	9.0	0.95			
1976	10.0	0.96			
1979	2.0	0.66			
1979	3.0	0.74			
1979	4.0	0.86			
1979	5.0	0.88			
1979	6.0	0.99			
1979	7.0	1.21			
1981	2.0	0.97			
1981	3.0	0.79			
1981	4.0	0.92			
1981	5.0	0.92			

Concentrations of Hg in smallmouth bass for the period of 1974 to 1994
(R. Sloan, NYS Department of Environmental Conservation, unpublished data)

Year	Age	Hg (μg/g)	Year	Age	Hg (μg/g)
1974	2.0	0.38	1985	5.0	1.13
1974	3.0	0.66	1985	6.0	1.37
1974	4.0	0.93	1985	7.0	0.85
1974	5.0	1.16	1985	8.0	1.34
1974	6.0	1.09	1985	9.0	0.76
1975	2.0	0.34	1985	10.0	1.08
1975	3.0	0.81	1985	11.0	1.77
1975	4.0	1.20	1986	2.0	0.90
1975	5.0	1.42	1986	3.0	0.85
1975	6.0	1.40	1986	4.0	0.93
1979	4.0	0.59	1986	5.0	1.18
1979	5.0	0.61	1986	6.0	1.47
1979	6.0	0.69	1986	7.0	1.19
1979	7.0	0.77	1987	3.0	1.46
1979	9.0	1.03	1987	4.0	1.61
1981	3.0	0.71	1987	5.0	1.74
1981	4.0	1.03	1987	6.0	1.78
1981	5.0	1.31	1987	7.0	1.87
1981	6.0	1.31	1987	8.0	2.13
1981	7.0	1.30	1987	9.0	2.29
1981	8.0	1.31	1988	3.0	1.10
1981	9.0	1.38	1988	4.0	1.11
1983	3.0	0.64	1988	5.0	1.42
1983	4.0	0.85	1988	6.0	1.81
1983	5.0	0.81	1988	7.0	1.86
1983	6.0	1.08	1988	8.0	1.42
1983	7.0	1.33	1989	3.0	1.33
1983	8.0	1.41	1989	4.0	1.61
1983	9.0	1.71	1989	5.0	2.13
1983	11.0	1.77	1989	6.0	2.67
1984	3.0	0.68	1989	7.0	2.34
1984	4.0	0.74	1990	3.0	1.02
1984	5.0	0.94	1990	4.0	1.05
1984	6.0	0.92	1990	5.0	1.20
1984	7.0	1.19	1990	6.0	1.00
1984	8.0	1.26	1990	7.0	1.70
1984	9.0	1.20	1990	8.0	2.54
1984	10.0	1.26	1990	9.0	2.14
1984	11.0	1.08	1991	4.0	0.67
1985	3.0	0.64	1991	5.0	0.73
1985	4.0	0.89	1991	6.0	0.81

Year	Age	Hg (µg/g)
1991	7.0	0.94
1991	8.0	79
1991	9.0	1.40
1991	10.0	2.33
1991	11.0	2.17
1992	3.0	0.52
1992	4.0	0.60
1992	5.0	0.72
1992	6.0	0.83
1992	7.0	0.85
1992	9.0	2.10
1992	10.0	2.62
1994	3.0	0.61
1994	4.0	0.64
1994	5.0	0.80
1994	6.0	0.90
1994	7.0	1.02
1994	**8.0**	**1.40**

Appendix VI

Simulated TSS mass fluxes for the epilimnion of Onondaga Lake
(in kg/year)

Scenario	Settling	Burial	Resuspension	Mineralization
1.1	3.1E+07	1.3E+06	2.9E+07	1.3E+06
1.2	3.1E+07	1.3E+06	2.9E+07	1.3E+06
1.3	3.1E+07	1.3E+06	2.9E+07	1.3E+06
1.4	3.1E+07	1.3E+06	2.9E+07	1.3E+06
1.5	3.1E+07	1.3E+06	2.9E+07	1.3E+06

Scenario	Settling	Burial	Resuspension	Mineralization
2.1	3.1E+07	1.3E+06	2.9E+07	1.3E+06
2.2	3.1E+07	1.3E+06	2.9E+07	1.3E+06
2.3	3.1E+07	1.3E+06	2.9E+07	1.3E+06
2.4	3.1E+07	1.3E+06	2.9E+07	1.3E+06
2.5	3.1E+07	1.3E+06	2.9E+07	1.3E+06
2.6	3.1E+07	1.3E+06	2.9E+07	1.3E+06
2.7	1.3E+07	1.3E+06	1.3E+07	1.3E+06
2.8	4.7E+07	1.3E+06	4.4E+07	1.3E+06

Scenario	Settling	Burial	Resuspension	Mineralization
3.1	3.1E+07	1.3E+06	2.9E+07	1.3E+06
3.2	4.7E+07	1.8E+06	4.3E+07	2.0E+06
3.3	2.6E+07	1.1E+06	2.4E+07	1.1E+06
3.4	1.6E+07	5.4E+05	1.4E+07	7.2E+05

Simulated TSS mass fluxes for the hypolimnion of Onondaga Lake
(in kg/year)

Scenario	Settling	Burial	Resuspension	Mineralization
1.1	3.7E+07	6.8E+06	3.0E+07	5.4E+05
1.2	3.7E+07	6.8E+06	3.0E+07	5.4E+05
1.3	3.7E+07	6.8E+06	3.0E+07	5.4E+05
1.4	3.7E+07	6.8E+06	3.0E+07	5.4E+05
1.5	3.7E+07	6.8E+06	3.0E+07	5.4E+05

Scenario	Settling	Burial	Resuspension	Mineralization
2.1	3.7E+07	6.8E+06	3.0E+07	5.4E+05
2.2	3.7E+07	6.8E+06	3.0E+07	5.4E+05
2.3	3.7E+07	6.8E+06	3.0E+07	5.4E+05
2.4	3.7E+07	6.8E+06	3.0E+07	5.4E+05
2.5	3.7E+07	6.8E+06	3.0E+07	5.4E+05
2.6	3.7E+07	6.8E+06	3.0E+07	5.4E+05
2.7	1.9E+07	6.8E+06	1.1E+07	5.4E+05
2.8	5.6E+07	6.8E+06	4.9E+07	5.4E+05

Scenario	Settling	Burial	Resuspension	Mineralization
3.1	3.7E+07	6.8E+06	3.0E+07	5.4E+05
3.2	5.6E+07	7.7E+06	4.8E+07	5.4E+05
3.3	3.1E+07	4.3E+06	2.6E+07	3.6E+05
3.4	1.9E+07	2.5E+06	1.6E+07	1.8E+05

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